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PROCEEDINGS

OF THE

AMERICAN ACADEMY OF ARTS AND SCIENCES.

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PROCEEDINGS

OF THE

AMERICAN ACADEMY

OF

ARTS AND SCIENCES.

VOL. XXXI.

PAPERS READ BEFORE THE ACADEMY.

Aid in the work described in this Paper was given by the Academy from the C. M. Warren Fund for Chemical Research.

I.

CONTRIBUTION FROM THE CHEMICAL LABORATORY OF CASE SCHOOL OF APPLIED SCIENCE.

XX. — ON THE COMPOSITION OF THE OHIO AND CANADIAN SULPHUR PETROLEUMS.

By Charles F. Mabery.

Presented October 10, 1894.

Notwithstanding the great number of investigations that have been undertaken on petroleums from different countries, our knowledge of their composition, especially of the portions with high boiling points, is still incomplete. What is known concerning American petroleums is based chiefly on the results of investigations which were carried on thirty years ago, before the discovery of several series of organic compounds, since shown to be contained in certain petroleums. With these facts in view, and having found in the study of the sulphur compounds from Ohio and Canadian petroleums that these oils are in certain respects peculiar in their composition, I have undertaken a comprehensive examination of them with reference to the different series of products which they may be found to contain. The study of Ohio petroleum seemed especially inviting on account of its origin in the Trenton limestone, a new horizon for a prolific oil supply, and its associations with animal remains in the oldest geological forma-

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tions of the continent. A similar interest attaches to the Canadian petroleum from the Corniferous limestone, which has yielded since 1862 enormous quantities of oil within the limited areas, less than thirty square miles, at Petrolia and Oil Springs. From the information already acquired concerning the nature of the sulphur petroleums, they seem to possess, beside their distinctive characteristics due to sulphur constituents, qualities of other petroleums which differ essentially in their composition.

In the earlier attempts to ascertain the constituents of petroleum, the methods then employed for fractional distillation were so inadequate that very little was accomplished. In 1862 the first systematic examination of American petroleum was undertaken by Pelouze and Cahours,* who showed the presence of the series of hydrocarbons C_nH_{2n+2}, beginning with butane. On account of a want of suitable apparatus for fractional distillation, their results lacked precision, and the questionable assumption was based upon them that petroleum is composed principally, including the heavier oils and paraffine, of the homologues of marsh gas. In accordance with the suggestion of Watts, these bodies were called the paraffine hydrocarbons, and as such they have since been known in chemical literature. Having obtained from coal oil a series of hydrocarbons corresponding to certain members of the series discovered by Pelouze and Cahours, Schorlemmer† submitted the more volatile portions of American petroleum to distillation, and succeeded in separating hydrocarbons that had not been recognized by Pelouze and Cahours. In a more thorough and carefully conducted examination of Pennsylvania petroleum, carried on contemporaneously with the investigations of the chemists mentioned above, by means of an efficient fractional condenser devised especially for this and other similar investigations, C. M. Warren‡ avoided the errors of other experimenters and established beyond question the presence in Pennsylvania oil of two series of hydrocarbons, each with an homologous difference in boiling points for CH_2 of 30°, and each member of one series differing in boiling point from the isomeric member of the other series by a little less than 8°. One of the series C_nH_{2n+2} identified by Warrren terminates at 127°.6, the other at 150°, the fractions of higher boiling points containing members of the series C_nH_{2n}. The assumption of Pelouze and Cahours that the frac-

* Comptes Rendus, LIV. 1241, LVI. 505, LVII. 62.

† Journ. Chem. Soc., 1862, p. 419.

‡ Mem. Amer. Acad. (N. S.), IX. 135; Proc. Amer. Acad., XXVII. 56.

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tions with higher boiling points have the composition represented by the general formula C_nH_{2n+2} was shown to be erroneous by the results of Warren, which excluded members of this series above 151°.

The presence of aromatic hydrocarbons in American petroleum was first recognized by Schorlemmer in 1865. Pelouze and Cahours had previously stated that American petroleum contained no aromatic hydrocarbons, but Schorlemmer collected a distillate from Canadian petroleum below 150°, and upon treating it with nitric acid and reducing with tin and hydrochloric acid, after distillation he obtained an oil with an odor of aniline that gave, with bleaching powder, the rosaniline reaction. The portion distilling between 150° and 170° gave a mixture of solid and liquid nitro-products, and the solid portion proved to be trinitrocumol. Benzol and its homologues were also found by Schorlemmer in Pennsylvania petroleum, in Galician petroleum by Freund* and others, and in Hanover petroleum by Bussenius and Einstuck.† In Galician petroleum Pawlewski‡ found two per cent of aromatic hydrocarbons, chiefly benzol and paraxylol, the latter never having previously been recognized in any petroleum. In the fraction 170°–190° from American kerosene, Engler§ discovered pseudocumol and mesitylene by the formation of nitro-compounds, and calculating the weight of crude oil corresponding to the weight of kerosene taken, it was estimated that these constituents are contained in crude Pennsylvania oil to the extent of 0.2 per cent. These hydrocarbons were also found in German, Galician, Italian, and Russian petroleum, in the latter to the extent of 0.1 per cent. According to the results of Beilstein and Kurbatoff,‖ the petroleum of the Central Caucasus has an essentially different composition from that of the deposits on the coast of the Caspian Sea. Oil obtained from the region of Zarskige Kolodzy, in the precinct of Tiflis in the Central Caucasus, proved to contain small amounts of benzol and toluol, but to consist principally, like the Pennsylvania petroleum, of the series C_nH_{2n+2}. Pentane, hexane, and heptane were identified. The oil from Baku on the coast contains the series C_nH_{2n+2} in smaller quantity, and Beilstein and Kurbatoff found no trace of the aromatic hydrocarbons C_nH_{2n-6}, but the principal constituents are members of the series C_nH_{2n}.

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* Ann Chem. Pharm., CXV. 19. † Ibid., CXIII. 151.
‡ Ber. der deutsch. chem. Gesellsch., 1885, p. 1915.
§ Ibid., 1885, p. 2234.
‖ Ibid., 1880, p. 1818; 1881, p. 1620.

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In Pennsylvania petroleum, Beilstein and Kurbatoff * recognized hexahydroisoxylol. In the fraction 95°–100° the same chemists detected the presence of a body containing less hydrogen than is required for the series C_nH_{2n+2}. Crude American heptane, when treated with nitric acid, gave a nitro-product corresponding to the formula $C_7H_{15}NO_2$. Nearly coincident with the researches of Beilstein and Kurbatoff, Schutzenberger and Jonine † identified, in the petroleum of Baku, hexahydrobenzol and hexahydrotoluol.

In their classic researches on the composition of the Caucasus petroleum, Markownikoff and Ogloblin ‡ showed the presence, in the oil from Baku, of benzol, toluol, isoxylol, pseudocumol, mesitylene, isodurol, durol, and higher hydrocarbons of the composition $C_{11}H_{14}$, $C_{12}H_{14}$, $C_{11}H_{12}$, and $C_{13}H_{14}$, and others, possibly homologues of styrol and phenylacetylene. Contrary to the experience of others, Markownikoff and Ogloblin found the naphtha from the Balachani plain on the Apscheron peninsula very rich in aromatic hydrocarbons; in the oil from the Central Caucasus, naphtenes were found to the extent of 80 per cent, and the aromatic hydrocarbons C_nH_{2n-6} to the extent of 10 per cent. At first Markownikoff looked upon the naphtenes as isomeric with the hexahydro compounds, but later Markownikoff and Spady § appear to accept the identity of octonaphtene and hexahydroisoxylol. ‖ As members of the naphtene series C_nH_{2n}, Markownikoff and Ogloblin identified hexahydromesitylene and the higher homologues between C_9H_{18} and $C_{15}H_{30}$. In petroleum from Boryslaw in Galicia, beside benzol, toluol, isoxylol, and mesitylene, Lachowicz ¶ found of the hexahydro series only hexahydroisoxylol.

The presence of unsaturated hydrocarbons C_nH_{2n} in American petroleum was not mentioned in the early publications of Pelouze and Cahours, nor were they referred to by Schorlemmer. Warren ** separated from Pennsylvania petroleum, rutylene, $C_{10}H_{20}$, boiling point 174°.9, margarylene, $C_{11}H_{22}$, boiling point 195°.8, and laurylene,

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* Ber. der deutsch. chem. Gesellsch., 1880, p. 2028.

† Comptes Rendus, XCI. 823.

‡ Ann. Chim. Phys., [6], II. 372.

§ Ber. der deutstch. chem. Gesellsch., 1887, p. 1850.

‖ In the Berichte, No. 7, April, 1895, recently received, the synthesis of 1–3-dimethyl hexamethylen, $C_6H_{10}(CH_3)$, is described by Zelinsky, and it is shown to be identical with the octonaphtene of Markownikoff, or hexahydroisoxylol.

¶ Ann. Chem Pharm., CCXX. 187.

** These Proceedings, XXVII. 56. Communicated May 12, 1868.

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$C_{12}H_{24}$, boiling point 216°.2. In an examination of a hydrocarbon naphtha obtained as a product of the destructive distillation of a lime soap prepared from menhaden oil, Warren and Storer * discovered the series C_nH_{2n+2}, beginning with C_5H_{12}, members of the aromatic series including benzol, toluol, xylol, and isocumol, and a series of the general formula C_nH_{2n} as follows: rutylene, $C_{10}H_{20}$, margarylene, $C_{11}H_{22}$, laurylene, $C_{12}H_{24}$, identical with the hydrocarbons previously separated by Warren from Pennsylvania petroleum. Warren and Storer also submitted Rangoon petroleum to prolonged distillation, and they succeeded in proving the presence in this oil of rutylene, margarylene, laurylene, cocinylene, and naphthalene.

As early as 1842, Pelletier and Walther separated a hydrocarbon from the "steinöl" of Amiano boiling at 80°–88°, to which they assigned the formula C_7H_{14}. A similar product with the properties of heptylene was obtained by Mabery and Smith † as one of the products in the sulphuric acid extract from the refining of Ohio burning oil distillate.

More recently Engler ‡ subjected menhaden oil to distillation under a pressure of ten atmospheres, and from the distillates thus obtained hydrocarbons were separated which proved to be identical with those contained in natural petroleum. These products included the light constituents of gasoline, the hydrocarbons of which burning oil is composed, the heavy oils, and paraffine. Engler, therefore, believes in the origin of petroleum from the decomposition of animal remains. The hydrocarbons distilling above 160°, referred by Pelouze and Cahours to the series C_nH_{2n+2} may really be naphtenes or similar bodies. In most petroleums more recently examined, it is believed that the unsaturated hydrocarbons are not present in the crude oil, but when found in the products of distillation have resulted from decomposition. Beilstein and Kurbatoff stated that the series C_nH_{2n} in the Caucasus petroleum does not consist of the homologues of ethylene. In the lower fractions of Galician oil, Lachowicz obtained no reaction with bromine even after long standing. Above 200° the ready absorption of bromine indicated the presence of unsaturated hydrocarbons; but it was attributed to decomposition. On the other hand, Engler § found that petroleums from Alsace (Pechelbronn), Oelheim (Hanover),

* Mem. Amer. Acad. (N. S.), IX. 177.
† These Proceedings, XXV. 222.
‡ Ber. der deutsch. chem. Gesellsch., 1888, p. 1816.
§ Zeit. Ang. Chem., 1888, p. 73.

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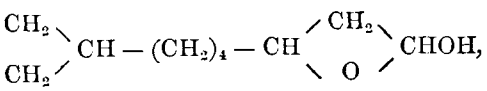
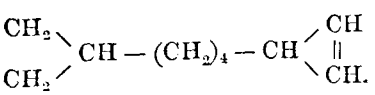
Tegernsee, Pennsylvania, Galicia, and Baku contain members of the series C_nH_{2n+2} and C_nH_{2n}, both unsaturated hydrocarbons and naphtenes. Engler asserts that all petroleums have the same composition, differing only in the proportions of their constituents. Markownikoff and Ogloblin * suggest the presence of unsaturated aromatic hydrocarbons in the oil from Baku.

Most analyses of crude petroleum have fallen short of 100 per cent, and the deficiency has been attributed to the presence of oxygen. In ascertaining the composition of oils from different districts, St. Claire Deville † showed that the percentage of oxygen varies between 2.1 per cent in the Canadian petroleum and 5.6 per cent in the oil from Zante. In 1874 Heil and Medinger ‡ attempted to separate acids from crude petroleum by agitating it with a solution of sodic hydrate and precipitating with sulphuric acid. The oil which separated was distilled and converted into a methyl ether. By saponification of this ether an acid was obtained to which was assigned provisionally the formula $C_{11}H_{20}O_2$. From the sodic hydrate solution used in the refining of Baku oil, by the addition of sulphuric acid, Aschan § separated a mixture of acids, and, taking advantage of a difference in solubility of their salts, he obtained one acid, $C_8H_{14}O_2$, distilling at 237°–239°, and another, $C_9H_{16}O_2$, that distilled at 251°–253°. The first acid, called by Aschan *octonaphtenecarboxylic acid*, by distillation with hydriodic acid, was converted into hexahydroisoxylol.

The oxygen compounds in petroleum were considered by Zaloziecki ‖ to be lacto-alcohols which are oxidized to acids by contact with air. By the same method which was followed by Heil and Medinger, and Aschan, Zaloziecki obtained an acid, $C_{10}H_{18}O_2$, to which he gave the formula,



and to the hydrocarbon obtained by distillation with hydriodic acid he gave the formula,



* Ber. der deutsch. chem. Gesellsch., 1883, p. 1873.

† Comptes Rendus, LXVI. 442; LXVIII. 485.

‡ Ber. der deutsch. chem. Gesellsch., 1874, p. 1216.

§ Ibid., 1890, p. 867; 1891, pp. 1864, 2710; 1892, p. 3661.

‖ Ibid., 1891, pp. 796, 1808.

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Engler looks upon these acids as formed by oxidation of other constituents of the crude oil. According to the results of Markownikoff and Ogloblin,* the fraction 75°–85° from Caucasus oil contains 0.76 per cent of oxygen compounds, and the fraction 220°–230°, 5.21 per cent. These oxygen compounds are in part acid, in part neutral, and in part phenol. The acids $C_{10}H_{19}COOH$ and $C_{11}H_{21}COOH$ were obtained as colorless oils; † Markownikoff and Ogloblin regarded these substances as naphtene carboxylic acids.

Most petroleums have been shown by analysis to contain nitrogen, usually in minute quantities. In distillates from Pennsylvania oil, Beilby ‡ found 0.08 per cent in the residuum or tar, and 0.375 per cent in the coke. Since the tar was one tenth of the crude oil, the latter contained 0.008 per cent of nitrogen. In crude Russian oil Beilby found 0.05 per cent. Peckham § found in West Virginia oil 0.54 per cent, in Mecca oil, 0.23 per cent, and in California oil, 0.56 – 1.1 per cent of nitrogen. In Egyptian oil, Kast and Kunkler ‖ reported 0.3 per cent of nitrogen, 1.21 per cent of sulphur, and 0.92 per cent of oxygen. Weller ¶ detected certain alkaloid bases in paraffine oil, and Bandrowski ** described a thick, transparent liquid solidifying at 20°, which he obtained by agitating Galician oil during several weeks with sulphuric acid. This substance gave a platinum salt containing 19.7 per cent of platinum. Upon neutralizing a sulphuric extract obtained in refining with calcic hydrate and distilling with steam, Zaloziecki †† obtained an oil containing nitrogen that formed a platosochloride whose percentage composition corresponded with that of tetrahydrocorridine $(C_{10}H_{19}NCl)_2PtCl_2$, or to the formula $(C_{10}H_{21}NCl)_2PtCl_2$; another insoluble platoso compound was shown by analysis to have the composition represented either by the formula $(C_{10}H_{15}NCl)_2PtCl_2$ or $(C_{10}H_{17}NCl)_2PtCl_2$.

Several hydrocarbons have been described as occurring in the less volatile portions of American petroleum. Hemilian ‡‡ obtained from the high boiling fractions "petrocene," a crystalline body melting

* Ann. Chim. Phys., [6.], II. 372.
† Ber. der deutsch. chem. Gesellsch., 1883, p. 1873.
‡ Journ. Soc. Chem. Ind., 1891, p. 120.
§ Geological Survey of California, Appendix to Vol. XL., p. 89.
‖ Chem. Centralb., 1890, p. 932.
¶ Ber. der deutsch. chem. Gesellsch , 1887, p. 2097.
** Monatsheft für Chem., VIII. 224.
†† Ibid., XIII. 498.
‡‡ Ber. der deutsch. chem. Gesellsch., 1876, p. 1604.

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above 300°. To this substance was assigned the formula $C_{32}H_{22}$. Prunier and David * stated that they had obtained evidence of the presence in refinery residues of anthracene, chrysene, pyrene, phenanthrene, chrysogene, retene, benzerythrene, fluoanthrene, parachrysene, paraanthracene, an isomeric acenaphtylene, besides different paraffines and stilbene. In the "petrocene" and "carbopetrocene" prepared from the tarry residue of petroleum, Prunier and David identified compounds, the former melting at 160°–190°, the latter at 200°–238°, and also thallene melting at 110°. They attributed the green fluorescence in petroleum to the presence of chinones. Inasmuch as these products were obtained from the distillation of tar in coking, evidently no inference is permissible concerning their presence in the crude oil. From "petrocene," Sadtler and McCarter † separated two hydrocarbons, one of which melted at 280° and the other at 178°. From these hydrocarbons the chinones were prepared, and from one an alizarine.

In undertaking an examination of the Ohio and Canadian sulphur oils with the advantage of former experience in studying the sulphur constituents, it was evidently necessary to conduct the distillations with all possible precautions to avoid decomposition. The tendency of the sulphur oils to decomposition by heat is due as much at least to the action of air on the hot oil as to the increased temperature. Markownikoff and Ogloblin attributed the decomposition in the distillation of the Russian oil to polymerization of the unsaturated compounds, and perhaps also to the polymerization of certain aromatic compounds, such as phenylacetylene, and they found that coloration of distillates on standing was less marked when the oxygen compounds had been removed. This tendency towards polymerization in unsaturated hydrocarbons separated from sulphuric acid solutions was observed by me, ‡ and it will receive further attention. It was therefore deemed advisable to carry on all distillations from the crude oils, instead of relying upon refinery products, except only the most volatile distillates, and the advantage gained has been apparent in subsidiary distillations of refinery oils which had been subjected to the decomposition incident to refinery distillation. Longer time is then necessary for separations, and the odor of decomposition is retained indefinitely during subsequent distillations. Certain constituents of the sulphur petroleums are even more unstable than the sulphides, as

* Bull. Soc. Chim., [2.], XXXI. 158.
† Amer. Chem. Journ., 1879, p. 30.
‡ Ibid., 1893, p. 92.

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shown by the rapid coloration of the oils when distilled, even after removal of the sulphides by mercuric chloride. Nevertheless, in the separation of constituents requiring larger quantities of distillates than can conveniently be collected *in vacuo*, since only porcelain or earthen ware stills are admissible on account of the decomposition in metallic stills, it may be necessary to depend to a limited extent upon refinery distillates.

After the first distillation of the crude oils *in vacuo*, distillation of the portion collected below 150° was continued under atmospheric pressure, since it occasioned no appreciable decomposition. Under the diminished pressure some loss of the constituents with low boiling points could not be avoided; but this was not important, since refinery distillates could be utilized for the separation of the volatile hydrocarbons. Distillation of considerable quantities of oil *in vacuo* presented certain difficulties. Neither glass nor metallic stills were suitable, and no American earthen ware stills could be procured that would support a vacuum on account of porosity from imperfect moulding and glazing. Some of the English earthen ware has supported a vacuum, but the ideal stills for such work, or for any distillations in large quantities, when metals cannot be employed, are those manufactured in the Royal Berlin Porcelain Factory. We have had a three-gallon porcelain still and several others of smaller capacity in operation almost continuously during several months with apparently no deterioration. When these stills are enclosed within a brick chamber, the temperature of distillation may, without difficulty, be carried above 350° by means of large laboratory burners. Another serious obstacle immediately presented itself in the porosity of common corks, which alone could be used for connections. After much labor it was found that tight joints could be secured by means of a rubber lute made by dissolving gum rubber in very light gasoline. Thin films of this lute drawn by the inward pressure into the joints and imperfections in the corks, after several applications, formed sufficiently close connections. Any other than the lightest gasoline as a solvent leaves a sticky film that is unpleasant to manipulate.

An important feature in prolonged fractional distillations *in vacuo* is a simple and convenient means for maintaining, without too close attention, a constant tension within the still. Air must not come in contact with the hot oil or vapor, and it would require too large quantities of an inert gas. An expedient suggested itself in the fact that occasionally small leaks held the manometer column stationary at whatever height it happened to stand. It therefore seemed possible to

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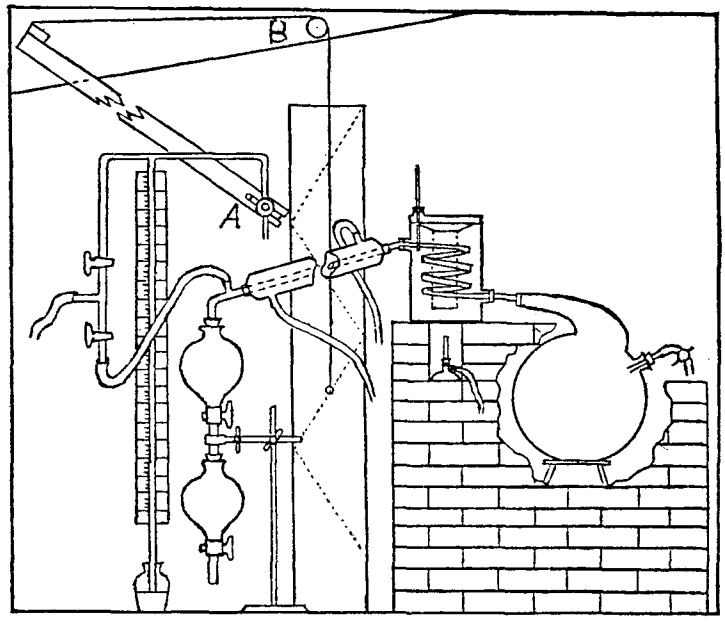
graduate leaks apart from the still in such a manner that the tension could be held constant for some time at any desired point.

The accompanying figure represents the form of regulator that has been used in all our distillations of large as well as small quantities of oils, together with the complete apparatus in the form for use. The regulator consists simply of a glass stopcock, A, better of considerable size, attached to the manometer by means of a side tube. To regulate closely the inflow of air an arm three to five feet in length,



according to the working of the stopcock, is attached firmly to the head of the cock, and supported in a manner easily movable within very small divisions on the arc of a circle of which it is the radius. To enable the operator to make adjustments while standing in front of the manometer, a piece of lead is attached as a weight to the upper end of the lever, and a cord is carried over a pulley, B. and terminates in a ring in front of transverse rows of pins a few millimeters apart. For economy of space the pulley is placed lower in the figure than its actual position. The upper part of the lever consists of two strips of wood, with a space between, through which passes a rigid copper wire as a support and guide. With the lever in a vertical position, the

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stopcock is fully open; any adjustment is easily obtained, and the manometer may be held stationary within one millimeter at any desired point during several hours.

In the distillation of small quantities of liquids requiring constant attention, we have used a piece of glass tube forty-five to sixty millimeters long, attached to the side stopcock, with a sliding support near the end. In vacuum distillations on a large scale it is more convenient to refer to the entire length of the manometer column, since at any time leaks may occur that are indicated only on the lower portion of the graduated scale. With a short manometer column alone, much time may be lost in waiting for an exhaustion that is interfered with by leaks.

In heating the still, direct contact with the flame was prevented by maintaining an air space above the burner by means of a sheet of asbestos. With such application of heat equally on the sides and bottom, there was less danger of decomposition at high temperatures. All but the highest distillates were collected in a Warren hot condenser containing a glass worm. With this condenser vacuum distillations are easily controlled, and, as in distillations under atmospheric pressure, with a great economy in time. Continuous distillation is possible without losing the vacuum, by drawing in consecutive fractions through the rear tubulure of the retort. The two receivers shown in the figure are convenient, and some additional advantage would be gained by means of an independent vacuum connection with the lower receiver. Several supports are not represented in the figure. Much time and tedious labor were expended on this apparatus before all the difficulties were overcome; but the compensation was ample, since by means of it we have been able to separate in considerable quantities constituents of high boiling points without decomposition, which otherwise would have been impossible. As an evidence of its usefulness, during several months continuous distillations were in progress, in charge of assistants, with highly satisfactory results. Distillates were collected at intervals of 10°, 5°, and 2°. The depression in boiling points by the diminished pressure in vacuum distillation varies between 60° and 65° for the lower constituents, and 125° or more for those collected between 300° and 350°. The residue above 350° (450°–500° atmospheric pressure) in both Ohio and Canada oils had apparently undergone but little decomposition; in appearance, it was a thick, ready flowing oil, with scarcely any odor.

A portion of the residual oil above 350° *in vacuo* was redistilled in an ordinary boiling flask, and the temperatures of the vapor and of

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the liquid were read on a Mahlke 550° thermometer. The oil began to distil with much decomposition at 385° in the vapor, and 415° in the liquid. One half distilled with the temperature in the liquid below 430°. Doubtless the temperatures of distillation were much reduced by the decomposition. Since we have found that distillations below 250° may be carried on successfully without serious decomposition in an atmosphere of carbonic dioxide, when we return to the distillation of the higher constituents this method may be serviceable.

Ohio Petroleum.

In the study of Ohio petroleum I have been aided by Mr. E. J. Hudson.* Besides the publications from this Laboratory on the sulphur compounds † and those of Orton, ‡ I am aware of no published statements concerning the composition of Ohio sulphur petroleum. The crude oil which formed the basis of our work was received from the Peerless Refining Company, Findlay, which controls a large section of oil territory. When received, it was of a somewhat thicker consistency than ordinary Pennsylvania oil, with a slight odor of hydric sulphide that is usually observed in crude sulphur oils. It contained a small quantity of water, which was removed completely only after long standing with fused calcic chloride. In determining the specific gravity of Ohio sulphur petroleums, oils were collected from wells at different points in the Findlay and Lima fields. The determinations were made at 20°.

Findlay Field.

	Specific Gravity.
(1) Barnsville	0.8272
(2) Heilstone Oil Co., Well No. 2, Hancock County	0.8296
(3) Ohio Oil Co., Wood County	0.8194
(4) Langmade Well, No. 4, Portage, Hancock County	0.8149
(5) Peerless Refining Co., Well No. 2, Liberty, Hancock County	0.8278
(6) Peerless Refining Co., Well No. 5, Baltimore, Wood County,	0.8239

* A part of this work formed the subject of a thesis by Mr. Hudson for the degree of Bachelor of Science

† These Proceedings, XXV. 218; Amer. Chem. Journ., XVI. 83.

‡ Ohio State Geological Reports, 1886, 1888, 1890; U. S. Geological Report, 1886–87.

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Lima Field.

The following specimens of crude oil, representing different portions of the Lima and Findlay fields, were received from the Ohio Oil Company, with a history of each well: —

	Township.	County.	Drilled.	Sand.	Oil.	Depth.	Production after shot.	Production at present.
				ft.	ft.	ft.	Daily.	Daily.
(1)	St. Mary's	Auglaize	May, 1892	1132	1147	1166	100 bbls.	5 bbls.
(2)	Liberty	Hancock	Aug., 1893	1250	1273	1286	75 "	10 "
(3)	Montgomery	Wood	Oct., 1892	1192	1197	1242	25 "	5 "
(4)	Woodville	Sandusky	July, 1892	1180	1195	1205	125 "	10 "
(5)	Nottingham	Wells, Ind.	April, 1895	990	1004	1044	165 "	75 "
(6)	Liberty	Wood	Sept., 1894	1152	1172	1227	125 "	30 "
(7)	Lima	Allen						

	(1)	(2)	(3)	(4)	(5)	(6)	(7)
Sp. gr.	0.8288	0.8345	0.8265	0.8254	0.8244	0.8428	0.851

There is evidently an appreciable variation in the composition and properties of the oils from different points in the Ohio field. Marked differences occur in the specific gravity as well as in the percentages of carbon, hydrogen, nitrogen, and sulphur.

The oil that was employed in this examination was somewhat heavier, with a specific gravity 0.8380. These results show an appreciable variation even in different portions of the same field. A similar variation in specific gravity has been observed in other fields: —

	Specific Gravity.
Alsace (Pechelbronn), depth 146 feet (Engler)	0.906
" " " 213 " "	0.885
Oelheim (Hanover) "	0.889
Tagernsee "	0.815
Pennsylvania "	0.8185
" "	0.801
Galicia "	0.8235
Baku "	0.859
" "	0.810
Ohio (Mabery)	0.838

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		Specific Gravity.
Ohio	(Markownikoff and Ogloblin)	0.887
Baku (Apscheron)	" " "	0.855–0.885
Galicia	" " "	0.835–0.895
American Petroleum	(Petrolitz)	0.830
" "	(Weil)	0.827
Canada	(Markownikoff and Ogloblin)	0.828
"	" " "	0.844
Alsace (Pechelbronn)	" " "	0.668

The value 0.887 assigned by Markownikoff to Ohio oil is much higher than has elsewhere been given. It must have been obtained in an oil from another Ohio field, perhaps from the Mecca district. The values given by Markownikoff for Canada oil must refer to a product from the Oil Springs district, although the number 0.828 is lower than is usually found even in that oil. The numbers given by Redwood are 0.844–0.854 for Oil Springs oil, and 0.859–0.877 for Petrolia oil. In Oil Springs oil we found 0.8427–0.8389 (gas oil), 0.8442, and in Petrolia oil, 0.8553, 0.8621, 0.8800.

In ascertaining the quantity of sulphur by combustion in air in the crude oil from which distillates were prepared for examination, the following results were obtained: (1) 0.73 per cent, (2) 0.72 per cent, (3) 0.72 per cent. In oils previously examined the percentage of sulphur has not been above 0.60 per cent. Sulphur was also determined in the oils collected in the Findlay and Lima districts in the order of the numbers given above: —

	Findlay.	Lima and Findlay.		Findlay.	Lima and Findlay.
(1)	0.33	0.61	(5)	0.68	0.56
(2)	0.63	0.71	(6)	0.61	0.76
(3)	0.56	0.37	(7)		0.81
(4)	0.68	0.49			

In Apscheron oil, Markownikoff and Ogloblin * obtained 0.064 per cent, and 0.16 per cent in Trans-Caspian oil.

The percentages of carbon and hydrogen in the oil from which distillates were obtained were found by combustion in air with a layer of plumbic peroxide in front to retain the sulphur †: carbon, 84.57; hydrogen, 13.62. In other samples from Findlay and Lima carbon and hydrogen were also determined: —

* Ann. Chem. Phys., [6.], II. 393. † Warren, These Proceedings, VI. 472.

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	Findlay.		Lima and Findlay.	
	C.	H.	C.	H.
(1)	85.76	13.56	84.73	13.48
(2)	85.82	13.80	84.03	13.05
(3)	84.33	13.46	83.89	13.18
(4)	84.35	13.36	84.55	13.55
(5)	84.20	13.41	83.41	13.13
(6)	84.18	14.60	85.07	13.33
(7)			85.00	13.05

The percentages of carbon and hydrogen that have been found in analyses of oils from other deposits are given in the following table: —

	O.	H.	O.
Apscheron (Markownikoff and Ogloblin)	86.65	13.35	
" " " " "	87.01	13.22	
" " " " "	86.89	13.18	
Trans-Caspian (Markownikoff and Ogloblin)	86.75	12.19	
Egyptian (Kast and Kunkler) *	85.85	11.72	
Pechelbronn (Sainte-Claire Deville) †	85.7	12.00	2.3
Galicia (Sainte-Claire Deville) †	82.2	12.10	5.7
Rangoon (Sainte-Claire Deville) †	83.8	12.7	3.5

The following values represent the percentages of carbon and hydrogen in crude petroleum from other American oil fields: —

	O.	H.	O.
W. Virginia, Scioto Well (Peckham) ‡	86.62	12.93	
W. Virginia Cumberland Well (Peckham) ‡		13.38	
California oil (Peckham) ‡		11.82	
Mecca oil (Peckham) ‡	86.32	13.07	
Canada, Manitoulin (Deville) †	83.00	14.6	2.4
Canada, Petrolia (Deville) †	84.5	13.5	2.0
Canada West (Deville) †	79.4	14.1	6.5
Ohio oil (Deville) †	84.2	13.1	2.7
Pennsylvania oil (Deville) †	83.4	14.7	1.9
Pennsylvania oil (Deville) †	84.19	13.7	1.4

* Chem. Centralb., 1890, p. 932.
† Comptes Rendus, LXVIII. 485.
‡ Geological Survey of California, Vol. XI., Appendix, p. 39.

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In the crude oil used in this examination, and in the other specimens described above, nitrogen was determined by the Kjeldahl method, and several closely concordant results were obtained by combustion with soda lime; the former gave 0.11 per cent, and the other oils the following percentages: —

	Findlay.	Lima and Findlay.
(1)	0.26 per cent	0.068
(2)	(*a*) 0.023, (*b*) 0.023 per cent	0.047
(3)	0.21 per cent	0.054
(4)	0.13 "	0.049
(5)	0.35 "	0.060
(6)	0.08 "	0.056
(7)		0.024

The presence of nitrogen in Ohio and Canadian petroleum will receive further attention at the close of this paper in some observations on the origin of petroleum.

The bromine absorption in the crude oils was determined by the method described in Allen's Commercial Organic Analysis. A weighed quantity of the oil was allowed to stand in the dark with a slight excess of bromine dissolved in dry carbonic disulphide, and the portion not absorbed was titrated with standard solutions of sodic hyposulphite and iodine. The strength of the bromine solution was ascertained by parallel titrations. Approximately one per cent of hydrobromic acid is evolved in these determinations in crude oils.

	Findlay.	Lima and Findlay.		Findlay.	Lima and Findlay.
(1)	11.29	8.74	(5)	13.07	10.93
(2)	14.62	9.31	(6)	11.32	12.31
(3)	10.55	11.49	(7)		12.06
(4)	14.89	12.30			

A comparison of the bromine absorption of the sulphur oils with that of oils from other sources indicates that bromine absorption is independent of sulphur compounds, and a distinctive property of petroleums in general. The following determinations were made: —

Chinese petroleum	10.90 per cent
Italian petroleum	7.10 "
Macksburg, O., petroleum	9.74 "
Berea Grit, O., petroleum	10.71 "
California petroleum	9.88 "

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The quantities of bromine absorbed by distillates from the crude sulphur oil were also determined: —

Fraction.	Percentage of Bromine absorbed.
110°–150°	0.73
150°–220°	1.74
220°–257°	4.84
257°–300°	5.04
300°–330°	12.10
Residue	19.50

Throughout this investigation some reliance has been placed on the absorptive capacity for bromine of crude oils and distillates obtained from them as indicating a certain unsaturated condition. While it should be borne in mind that a considerable proportion of the bromine absorption is due to the sulphur constituents, there is besides a large absorption in the crude oils and in the residues of distillation above 350° by other constituents. There is much yet to be learned concerning the decompositions in distillations at high temperatures, which are indicated by the greatly increased bromine absorption, and the study of the higher boiling portions will be greatly facilitated by the aid of the Mahlke thermometers for observing temperatures below 550°.

The characteristic qualities of Ohio oil appear also in the proportions that distil at different temperatures; 800 grams of the crude oil collected in the following proportions beginning at 110° : —

	110°–150°	150°–220°	220°–257°	257°–300°	300°–350°	Residue.
Grams	76	133	86	76	69	348
Per cent	9.75	16.63	10.75	9.75	8.63	43.5
Sp. Gr. at 20°	0.7282	0.7669	0.7940	0.8138	0.8242	0.8976
Per cent sulphur	0.10	0.38	0.41	0.37	0.37	0.54

The distillates below 225° were colorless, and no odors resulting from decomposition were observed. Above this point color appeared in the distillates, with the odor of decomposition, which became more marked with increasing temperatures. Above 275° the heavier paraffine oils began to distil. In refinery distillation of Ohio petroleum it is therefore evident that cracking begins in the vicinity of 250°. No doubt crude sulphur petroleums undergo decomposition spontaneously to some extent, since upon standing they always contain hydric sulphide. We find that certain unstable constituents separated from the crude oils gradually become darker in color, with other indications of chemical change. At the beginning of the distil-

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lation hydric sulphide came off in considerable quantities, but after the first fraction very little appeared in the succeeding distillates below the point where decomposition began.

On account of the viscous character of the Ohio and Canadian petroleums, and the large proportion of heavy oils, temperatures indicated by the thermometer in the vapor of the distillates should he higher than the corresponding temperatures of the oil. To ascertain this difference, crude Findlay oil was distilled, and the temperatures of the distillates and of the oil were noted with the following results: —

Thermometer in the Oil.	Thermometer in the Vapor.	Difference.
°	°	°
167	120	47
180	140	40
203	160	43
221	180	41
238	200	38
259	220	39
282	240	42
301	260	41
318	280	38
341	300	41

Except in the first reading the average difference in temperature is about 40°.

Determinations of sulphur in the crude oil and in the distillates obtained from it, showed that considerable sulphur was lost during distillation. In order to obtain definite information concerning the quantity lost, 100 grams of the crude oil were distilled under atmospheric pressure, and attached to the receiver were flasks containing a solution of sodic hydrate for the purpose of absorbing any hydric sulphide that escaped. In front of the flask containing hydric sulphide there was connected another flask, which contained alcohol, with a delivery tube in front to absorb volatile products that might result from decomposition. The oil was fractioned to 300°, collecting between 115° and 250°, and between 250° and 300°, and the hydric sulphide was determined after oxidation with bromine by precipitation with baric chloride. The percentage of sulphur in the several fractions was also determined. As usual in distillation of the sulphur petroleums, a slight sublimate of sulphur was observed in the neck of the condenser. Upon diluting the alcohol it became slightly turbid, which indicated probably some volatilization of sulphur constituents.

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The alkaline solution of the sulphur from the distillate 115°–250° gave 0.1135 gram of baric sulphate, corresponding to 0.0156 gram of sulphur. From the alkaline solution of the sulphur absorbed from the fraction 250°–300°, 0.6946 gram of baric sulphate was obtained, corresponding to 0.0958 gram of sulphur. A determination of sulphur in the distillate 115°–250° gave 0.55 per cent; in the distillate 250°–300°, 0.51 per cent; and in the residue above 300°, 0.60 per cent. Since the weight of the distillate collected at 115°–250° was 20.55 grams, the weight at 250°–300°, 5.1 grams, and the weight of the residue above 300°, 74.35 grams, the total weight of sulphur accounted for in these determinations was 0.7166 gram, leaving 0.27 gram which must have escaped in ways not determined.

In comparing the quantities of the distillates from Ohio oil, and their specific gravities, with those obtained by Markownikoff and Oglobin * in the Apcheron oil with a specific gravity at 17° of 0.882, and those given by Bolley from Pennsylvania petroleum with a specific gravity of 0.816, it is evident that the properties of Ohio petroleum place it between the Caucasus and Pennsylvania oils.

The Caucasus oil began to distil at 120° in the vapor, and 180° in the liquid.

	Apscheron.		Pennsylvania.			Ohio.	
°	Parts in 100.	Sp. Gr.	Parts in 100.	Sp. Gr.	°	Parts in 100.	Sp. Gr.
120–150	0.5	0.786	19.70		110–150	9.75	0.7282
150–200	10.9	0.824	8.85	0.757	150–220	16.63	0.7669
200–250	12.8	0.861	15.23	0.788	220–257	10.75	0.7940
250–320	24.7		20.7	0.809	257–300	9.75	0.8138
					300–350	8.63	0.8242
Total	47.9		64.48			55.51	
Residue	53.1		35.52			43.00	

While the temperatures at which the Ohio oil was collected are slightly different from the others, they are sufficiently close for comparison.

Kramer † has compared the quantities of distillates obtained from crude petroleum of other fields: —

	Sp. Gr.	–150°	150°-250°	250°-300°	Residue.
Tagernsee	0.812	20.04	26.12	14.00	35.91
Pennsylvania	0.814	14.34	25.35	13.75	40.99
Baku	0.880	0.63	12.73	15.55	37.95
Oelheim	0.885	0.74	11.05	9.75	75.71
Alsace	0.888	1.3	16.37	17.07	47.88

* Ber. der deutsch. chem. Gesellsch., 1883, p. 1873.

† Chem. Centralb., 1887, p. 290.

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Taubes Barlâdu* distilled 1115 c.c. of crude Roumanian petroleum from the deposits on the south slope of the Carpathians, which are probably connected with the Galician oil zone, with the following results:—

°	c.c.	Per cent by Volume.
30–125	150	13.5
125–225	385	35.5
225–280	160	14.3
280–315	98	8.1

In an examination of Burmese petroleum, Romanis† obtained an oil from Yay-nan-Chaung with a specific gravity of 0.8590, which solidified at 24°. An oil from Arracan with a specific gravity of 0.825 at 32° contained considerable benzol and other aromatic hydrocarbons; upon distillation, the following results were obtained:—

	Per cent.	Distilled with Steam.	
		°	Per cent.
70–90	3.1	—100	23.3
90–100	7.6	100–110	33.0
100–130	10.6	110–130	29.3
130–200	18.7	Residue	13.3 (heavy oil)
200–300	18.7		98.9
+ 300	12.5		
Oil in residue	8.0		
Paraffine	3.1		
Loss	17.7		
	100.00		

Markownikoff and Ogloblin examined the ash of Caucasus petroleum by igniting the residue of distillation. They found 0.09 per cent of ash calculated for the original quantity of crude oil, and it consisted chiefly of the oxides of calcium, iron, and aluminum. Traces of copper and silver were also found. We have determined by combustion in oxygen the percentages of carbon and hydrogen in coke from the refinery residue of the distillation of Ohio petroleum; the per cent of carbon was 95.06, and that of hydrogen 4.85. A determination of nitrogen by the Kjeldahl method gave 0.31 per cent. The quantity of ash in the coke was determined by burning off the carbon, and the weight of ash thus obtained corresponded to 0.11 per cent of the coke burned. In attempting to estimate the percentage of ash in the crude

* Zeit. Ang. Chem., 1889, p. 606. † Chem. News, LIX. 292.

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oil from the amount found in the coke, there is some uncertainty as to the quantity of oil corresponding to the coke. In some oils the proportion of residue is estimated as ten per cent of the crude oil. It depends also upon the method followed by the refiner. Sometimes the first distillation of the crude oil is pushed to the point of complete decomposition, and the tar distillate is again distilled until it is coked. It is well known that earthy matter frequently remains for some time in suspension in the crude oil after it is taken from the wells. On this account, if the oil was distilled before the suspended material had subsided, the ash would not represent what had been in solution in the oil. But the oil is usually allowed to stand some time before distillation, and that the coke we examined was practically free from suspended matter is evident from the low percentage of ash, and corresponding results with Canadian oil where the ash was determined in a tar distillate and in coke from crude oil; the percentages of ash from the two sources were not very different.*

In Findlay oil, in which our determination was made, the proportion of still residue is doubtless somewhat smaller than that mentioned above, probably between ten and five per cent. The corresponding percentage of ash in the crude oil would, therefore, be not far from 0.005 per cent, an amount considerably less than Markownikoff and Ogloblin found in Russian oil.

An analysis of the ash showed that it was composed chiefly of lime and magnesia, and the quantity of magnesia is at least equal to that of the lime. Traces of iron and aluminum were found, the iron possibly having been dissolved from the still. It is therefore evident that the crude oil has exerted an appreciable solvent action on the limestone reservoir, dissolving both constituents of the dolomitic rock.

It is maintained by some chemists that all petroleums contain the same series of compounds in different proportions, and that the difference in properties depends upon a variation in the quantities of the constituents. In a general sense, with respect to the principal series of hydrocarbons this is doubtless true; yet there is such a wide difference in the properties of oils like those from Pennsylvania and the Caucasus that they are characteristic of substances quite unlike. The Caucasus petroleum is wholly, or nearly, wanting in the series C_nH_{2n+2}, and the Pennsylvania oil evidently contains the series C_nH_{2n} in much smaller proportion than the Russian oil. The presence of the higher members of the latter series in the Pennsyl-

* Determination of Ash in Canadian Petroleum, page 51.

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vania oil has yet to be ascertained. It is conceivable that the difference in the composition of petroleums is due to the different influences to which they have been exposed. Perhaps greater porosity of the reservoir or cover where oils exist under pressure has permitted an escape from certain oils of the more volatile constituents, especially of the series C_nH_{2n+2}. If this should be demonstrated by more extended observations, it would be reasonable to expect the same bodies in the Pennsylvania as in the Russian oil, only in smaller quantities of the higher constituents. Referring the sulphur in Ohio petroleum to the average composition of the compounds containing it, the crude oil should contain at least five per cent of the sulphur derivatives. Evidently such a large proportion of sulphur compounds in petroleum must exert an important influence on its properties, and we should therefore expect a marked difference between the sulphur petroleums and those which contain only traces of sulphur.

From a general similarity of Ohio petroleum to the oil from Pennsylvania, so far as it relates to hydrocarbons of the series C_nH_{2n+2}, it should perhaps be expected that the composition of the latter oil, which has been established beyond question, at least so far as the portions of low boiling points are concerned, should represent also similar portions of the Ohio product. As mentioned above, even a casual examination of the sulphur oils affords abundant evidence that their peculiar properties depend upon other constituents than the hydrocarbons C_nH_{2n+2}. While these unique constituents may detract from, rather than enhance, the value of the sulphur oils for commercial purposes, it is as important for the intelligent guidance of the refiner as it is interesting from a scientific point of view that they be well understood.

While occupied with the sulphur compounds in Ohio petroleum, I was impressed with the complexity in composition manifested by the products of distillation, and with the importance of a thorough examination for all constituents. We therefore began with an endeavor to separate and identify the individual homologues of methane which have been found in Pennsylvania petroleum, including an approximate quantitative determination of all but the more volatile members.

Hydrocarbons C_nH_{2n+2}.

To separate the hydrocarbons of lower boiling points we obtained twenty-five litres of the very first distillate from a three-hundred barrel still. This distillate contained 0.10 per cent of sulphur.

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Considerable gas always escapes in refinery distillation before a liquid distillate appears, but we have not yet undertaken an examination of its composition. Probably this is essentially the same as that of the gas given off in beginning a distillation of Pennsylvania oil together with hydric sulphide, which is always evolved to a greater or less extent in the distillation of sulphur petroleums. Sadtler* found that the gas from Pennsylvania wells consisted principally of methane, with some ethane, nitrogen, and hydrogen. In the gas from Canada wells, at Enniskillen, Fouqué† found marsh gas, ethane, and small quantities of carbonic dioxide. According to Ronalds,‡ the gas from Pennsylvania petroleum contains 1.27 per cent of carbonic dioxide, 6.58 per cent of oxygen, 54.00 per cent of nitrogen, and 38.15 per cent of ethane and propane; by exposing the escaping gas to a freezing mixture, butane was condensed to a liquid.

In an exhaustive study of natural gas from Pennsylvania wells, Phillips § found that the principal constituents were hydrocarbons C_nH_{2n+2}, with nitrogen in variable proportions and carbonic dioxide in small quantity, but no hydrogen nor carbonic oxide.

The crude distillate was subjected to fractional distillation in a porcelain still, to which was attached a Warren condenser filled with a mixture of salt and ice, with ice alone, or with water, according to the fraction collected. Another ordinary condensing worm surrounded with a freezing mixture was placed in front. Subsequent distillations were conducted in glass stills, and the fractions rapidly accumulated within limits of temperature which distinguish the hydrocarbons C_nH_{2n+2}. At the beginning of the first and second distillations, a delivery tube was attached to the bottle receiving the distillate, and extended so as to collect in a receiver inverted over water any volatile constituents that might have escaped condensation. At first a very little gas collected, which burned with a smoky flame, but none afterwards. The following quantities were collected during the first distillation: —

	−25°	25°-30°	30°-35°	35°-40°
Grams	525	400	450	400

After the fourth distillation thirty-five grams collected between 0° and 1°, distilling for the most part at 0°, barometer 740 mm. This was evidently butane, boiling point 0°. Inasmuch as the boiling point of

* Amer. Chemist, 1876, p. 97.
† Comptes Rendus, LXVII. 1045.
‡ Journ. Chem. Soc., XVIII. 54.
§ Amer. Chem. Journ., 1894, p. 406.

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this hydrocarbon has been carefully determined,* further examination was not deemed necessary. The temperature rose rapidly to 5°, and between 7° and 9° 20 grams of a distillate collected, mostly between 7° and 8°, the boiling point of a hydrocarbon which was separated by Warren from Pennsylvania petroleum, and which was regarded by him as one of the butanes. Since the atmospheric temperature was in the vicinity of 30° when these distillations were in progress, special care was necessary to preserve the distillates, and the ice accidentally becoming exhausted in the ice-chest, the distillate collected at 0° burst the bottle, and the one at 8° forced out the stopper and volatilized. Of the two possible butanes, the boiling point of one is without question 0°. The other seems to have been obtained by Butlerow † from isobutyl alcohol, and the boiling point assigned to it was —17°.5. Under more favorable conditions, we shall collect a larger quantity of this distillate, to determine by its chemical behavior, as well as by its constancy in boiling point, whether it be a definite compound.‡

Considerable quantities of distillates collected below 30°, but by continued distillation they were mostly separated into higher and lower constituents, indicating the absence of individual products. In the vicinity of 30° the fractions were large, amounting to 300 grams between 28° and 32°. After the ninth distillation, 75 grams collected between 29° and 30°, with the barometer at 747 mm. A vapor density determination gave 2.52, required for pentane 2.49. This product was, therefore, isopentane, boiling point 30°. Between 36° and 37°, 75 grams distilled, and this distillate was shown by its vapor density to have the composition required for pentane; a vapor density determination gave 2.49, required for pentane 2.49. This substance therefore corresponded to normal pentane, boiling point 37°

* Ronalds, Journ. Chem. Soc., XVIII. 54; C. M. Warren, Mem. Amer. Acad. (N. S.), IX. 156.

† Ann. Chem. Pharm., CXLIV. 10.

‡ We have since obtained 50 grams of an oil that collected at 8° to 9° with very small amounts above and below these limits. A vapor density determination by the Hofmann method gave the following result: —

0.0717 gram of the oil gave 45.5 c.c. of vapor at 16°, and under a tension of 48.1 cm. of mercury.

Required for C_4H_{10}.	Found.
2.01	2.04

For further proof as to the composition of this distillate, an examination of its halogen and other derivatives is now in progress.

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(Warren). The weights collected evidently afford no information concerning the proportions in which these hydrocarbons are contained in the crude oil. Other results show that they are present in smaller quantities than in Pennsylvania oil.

At higher temperatures to 60°, the weights of the distillates were very small and irregular, which indicated the absence of definite compounds. Between 60° and 62°, 150 grams collected at the end of the fifteenth distillation, and this was still further reduced to 50 grams between 60° and 61°, with a vapor density corresponding to that of hexane; found, 2.94; required for hexane, 2.98; boiling point of isohexane, 61°.27 (Warren). After the fourteenth distillation, with the barometer at 749 mm., between 67° and 68°, 75 grams collected that distilled tolerably constant within this limit. A vapor density determination gave 3.00; required for normal hexane, 2.98; boiling point, 68°.5 (Warren).

For the separation of the less volatile hydrocarbons, the fraction —150°, obtained from the crude oil by distillation *in vacuo*, was subjected to further distillation under atmospheric pressure. 41.5 kilos of crude Findlay oil were distilled under a tension of 50 mm., and collected in the first distillation at —100°, 100°–150°, 150°–200°, 200°–250°, and 250°–350°. The decomposition was comparatively slight, and the fractions, especially the less volatile, were free from the disagreeable pungent odors characteristic of refinery distillates. Even the residue above 350° had apparently undergone very little decomposition. On account of the reduced boiling points, it was not expected that the more volatile constituents could be collected, and it was subsequently found that scarcely any distillate boiling below 30° was condensed. The weights of the first fractions were as follows: —

	—100°	100°–150°	150°–200°	200°–250°	250°–350°	Residue.
Grams	8000	8520	6480	7700	2670	9000
Percentages	18.6	19.8	15.1	18.0	6.2	20.9

The specific gravity of the individual fractions was determined with the following results: —

—100°	100°-150°	150°-200°	200°-250°	250°-350°	Residue.
0.7445	0.7941	0.8245	0.8455	0.907	0.9139

The fraction —100° contained no hydric sulphide; the higher fractions contained it in small quantities. The percentages of sulphur in the same distillates were obtained by combustion in air: —

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	–100°	100°–150°	150°–200°	200°–250°	Residue.
Sulphur	0.054	0.25	0.42	0.61	0.67

In comparing the percentages of sulphur in the vacuum distillates with those under atmospheric pressure, it is evident that the main body of the sulphur compounds collects in the higher portions, leaving the fractions below 150° nearly free from sulphur.

Percentages of sulphur under atmospheric pressure: —

110°–150°	150°–220°	220°–257°	257°–300°	300°–350°	Residue.
0.10	0.38	0.41	0.37	0.37	0.54

It is also apparent that distillation *in vacuo* protects, to a certain extent, the sulphur compounds from decomposition. In ordinary distillation of the crude oil, as has been mentioned, sulphur is invariably observed in the condensing tube. Even in vacuum distillation at high temperatures decomposition cannot be wholly avoided, although the separation of sulphur has never been observed. It is probable that chemical reactions occur within the oil from the action of the various constituents upon one another, such, for example, as the action of the oxygen compounds upon the sulphur compounds. These observations are valuable evidence in favor of vacuum distillation for the sulphur petroleums.

The percentage of bromine absorbed by the fractions collected *in vacuo* was also determined: —

	–100°	100°–150°	150°–200°	200°–350°	Residue.	Crude Oil.
Bromine	0.0	4.57	6.60	7.08	24.38	10.19

It is interesting to compare the bromine absorption in the vacuum distillates with the quantities absorbed in the distillates collected under atmospheric pressure: —

	100°–150°	150°–220°	220°–257°	257°–300°	300°–330°	+330°
Bromine	0.73	1.74	4.84	5.04	12.10	19.50

Doubtless the larger absorption of bromine in the vacuum distillates at lower temperatures depends, at least in part, upon the fact that the sulphur compounds are protected from decomposition during distillation, and also upon the extent to which the constituents with higher boiling points are distilled at lower temperatures under the diminished pressure. It would be expected that the residue in the distillation under atmospheric pressure should show a higher absorptive power than that collected *in vacuo*. The behavior of the higher fractions

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toward bromine and the nature of the decompositions by cracking will receive further attention.

The portions distilling below 150° were next submitted to prolonged fractional separations under atmospheric pressure with the aid of Hempel columns and Warren condensers. We were led to appreciate the exhaustive labors of our predecessors in their investigations on petroleum, and our indebtedness to them for the efficient means at present available for conducting such distillations. For the separation of complex mixtures, especially in considerable quantities, in point of efficiency the Warren condenser leaves nothing to be desired. It appears to effect a more rapid separation than the Hempel column, although the latter is of great service. The Hempel method has the advantage that it requires less attention, with no loss of time in heating a bath nor in maintaining a constant temperature in the bath. From the description of Warren's hot condenser given in the treatise on Chemistry, Vol. III. Part 1, by Roscoe and Schorlemmer, an erroneous impression must have been received concerning this apparatus. On pp. 149, 150, the following words appear: "An apparatus has been employed by Warren in the fractional distillation of tar oils and petroleums. This permits a complete control over the temperature of the vapor, accomplished by an air bath round which a spiral tube is placed, connected with the boiling flask. The temperature of this air bath is regulated by a lamp. The liquid used for heating the air bath may be either water, oil, or fusible metal, and into this the thermometer is placed. . . . In distilling petroleum the difference in temperature between the boiling liquid and the air bath was, to begin with, about 35°, or even more." The idea conveyed here is that the constant temperature is maintained by means of an air bath, although it is evident from the following description, taken from the original memoir,* that there is not the remotest allusion to an air bath: "In the new process, perfect control of the temperature of the vapors is secured by simply conducting these vapors upwards through a worm contained in a bath the temperature of which is regulated by means of a lamp, or by a safety furnace. The bath may be of oil or water or metal for very high temperatures, as the case may require, and it is furnished with a thermometer. That this bath may be equally adapted for the separation of liquids boiling below the common temperature, an empty vessel is permanently secured in the interior of the bath by means of straps of metal across the top, to

* Mem. Amer. Acad. (N. S.), IX. 125.

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serve as a convenient receptacle for ice or ice water, by means of which a low temperature may be steadily maintained. This interior vessel also serves a good purpose in economizing time and fuel in heating the bath, as it diminishes the quantity of oil required to cover the worm. It is made to extend to within about three inches of the bottom of the bath, and large enough to fill a greater part of the space in the centre of the coil." It will therefore be seen that it was not Warren's intention to use this apparatus in any sense as an air bath. It is to be used solely as a liquid bath.

Since the principal object was to identify the individual constituents and to determine their approximate quantities, it was only necessary to collect our products within such close limits of temperature comparable with boiling points already accurately determined that they should yield satisfactory analytical data. In successive distillations, collecting at first within 5°, then within 2°, and finally within 1°, after the fifth distillation the fractions collected rapidly, with increasing quantities at temperatures near boiling points of well known hydrocarbons C_nH_{2n+2}, and at certain other points at which an equilibrium in boiling points seemed to be established by mixtures. It was only with much difficulty that some of these mixtures could be separated into their constituents. We had occasion to recall the remark of Warren concerning the greater amount of labor involved in determining the absence of definite compounds in such mixtures than in proving the presence of well defined hydrocarbons. The fractions containing the aromatic hydrocarbons will be considered together. The products collected for vapor density determinations were purified as completely as possible by the removal of unsaturated hydrocarbons, sulphur compounds, and the aromatic hydrocarbons. For the removal of sulphur compounds, each fraction was thoroughly agitated with alcoholic mercuric chloride. After washing with water, there remained in solution not more than 0.02 or 0.03 per cent of sulphur when the mercuric chloride gave a crystalline precipitate, which was the case in distillates below 150°, provided they were collected at first *in vacuo*. In a former paper * it was stated that alcoholic mercuric chloride removed two thirds of the sulphur. Those experiments were made with refinery distillates, which do not behave the same towards mercuric chloride as vacuum distillates. In higher fractions somewhat more sulphur is retained, and with increasing boiling points even the mercury itself in considerable quantity may be held in clear solution, either in the form of

* Amer. Chem. Journ., 1894, p. 88.

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$HgCl_2R_2S$, or in some other combination. This peculiarity has occasioned us much trouble in purifying distillates above 200°. In some of these products, hydric sulphide in the cold will not precipitate the mercury; frequently it is only after prolonged action with the aid of heat that the mercury can be completely removed. These sulphur oils seem to possess the property of dissolving metals, metallic oxides, and other compounds, which has been observed in other petroleums. The action of paraffine oils on metals has been examined by Macadam,* who finds that lead, solder, and zinc are quite readily, tin and iron but slightly, affected. Some oils have a greater solvent action than others, and Macadam attributes it to the hydrocarbons. Engler† repeated the experiments of Macadam, and observed that metals were not affected when air is excluded. It was therefore inferred that acid compounds are formed in the oil by exposure to air, and also metallic oxides, which are dissolved by the acids. Engler does not attribute the solvent action to ozone. It is probable that the purification of refinery distillates from the sulphur petroleums, by agitation with an alkaline solution of plumbic oxide, depends, at least in part, upon the solvent action of certain constituents of the oil. Oxygen compounds, which are doubtless present in these oils, may assist the action, as has been observed in other oils. This subject will receive further attention when we reach the higher distillates.

After removal of the sulphur compounds, each distillate for vapor density determination was thoroughly agitated, first with concentrated nitric, then with concentrated sulphuric acid, washed, and dried. Finally, under a return condenser, it was heated for some time with metallic sodium.

From 41.5 kilos distilled *in vacuo*, at the end of the eighth distillation, the last seven under atmospheric pressure, the following weights were obtained with much smaller quantities outside these limits: —

	—55°	58°-62°	65°-68°	77°-83°
Grams	15	120	310	85

As already mentioned, on account of loss from the diminished pressure, as well as the unavoidable loss in any distillation, the weights of the lower fractions collected *in vacuo* evidently cannot be accepted as representing even approximately the quantities present in the crude oil.

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* Journ. Chem. Soc., 1878, p. 355.

† Ber. der deutsch. chem. Gesellsch., 1878, p. 2186.

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Between 87° and 93°, 80 grams collected after the sixth distillation, and in the portion which distilled constant at 89°–90°, bar. 754 mm., a vapor density determination gave 3.43; required for isoheptane, 3.46; boiling point, 90°.4 (Warren).

At the end of the sixth distillation, 175 grams collected at 96°–99°, and 50 grams distilled constant at 96°–97°, bar. 744 mm.; a vapor density determination of this product gave 3.42; required for heptane, 3.6; boiling point of heptane, 98°.7 (Warren). Above this point the distillates were small in amount to 109°, where other products began to appear; between this limit and 120° the single degree fractions were considerable in quantity.

At 118°–120°, 120 grams were collected, of which 50 grams distilled constant at 119°–120°, bar. 749 mm. This product gave a value in a determination of its vapor density required for octane: found, 3.98; required, 3.94. Since some doubt has been expressed concerning the existence of an octane with this boiling point, this fraction was carefully purified for analysis with alcoholic mercuric chloride, nitric acid, and sulphuric acid, and it was finally submitted to prolonged boiling with sodium. Determinations of carbon and hydrogen then gave the following results: —

I. 0.1707 gram of the oil gave 0.5282 gram CO_2, 0.1707 gram H_2O.
II. 0.2017 gram of the oil gave 0.6237 gram CO_2, 0.2737 gram H_2O.

	Calculated for C_8H_{18}.	Found. I.	Found. II.
C	84.20	84.42	84.28
H	15.79	15.19	15.08

The low percentage of hydrogen evidently indicated that the octane was still contaminated by a hydrocarbon containing less hydrogen. For further purification the oil was heated to boiling during several hours with a mixture of nitric and sulphuric acids, and boiled several times with sodium. It then gave the percentages of carbon and hydrogen rquired for octane: —

	Required for C_8H_{18}.	Found.
C	84.20	84.20
H	15.79	16.10

There seems to be no question that the fraction 118°–119° contains a hydrocarbon with the composition required for octane, and this observation is apparently confirmed by the results of others. War-

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ren * separated a constituent of Pennsylvania petroleum distilling constant at 119°.5 (cor.), which gave a vapor density corresponding to that of octane. From the extraordinary care with which the determinations of Warren were made, there can be no doubt as to the existence of a hydrocarbon with this boiling point in Pennsylvania petroleum. Although hexahydroisoxylol has been recognized by Beilstein and Kurbatoff,† it is probably not the principal constituent with this boiling point of the Pennsylvania oil; it is certainly not of the Ohio oil.

From coal oil, Schorlemmer ‡ separated an octane boiling at 119°–120°, and subsequently he identified the same body in petroleum boiling at 119°. The following data are taken from his original publication: —

	Required for C_8H_{18}.	Found.
C	84.20	84.10
H	15.79	16.10
Vapor density	3.98	3.95

In the treatise on Chemistry by Roscoe and Schorlemmer, New York, 1886, it is stated that the three octanes known are normal octane, boiling point 125°.46, found in petroleum; tetramethylbutane, boiling at 108°.5; and hexamethylbutane, melting at 96°–97° and boiling at 105°–106°. This enumeration does not recognize an octane boiling at 119° in petroleum. It would seem that our fraction from the Ohio oil was prepared with sufficient care to preclude the possibility of a mixture of higher and lower constituents. We shall endeavor to obtain independent evidence as to the identity of this fraction by a study of its chemical reactions, and the preparation of its derivatives.

The following suggestion, which I have taken from one of the private papers, dated 1868, of Mr. Warren, through the kindness of Professor Storer, indicates that Warren recognized the possibility of a series containing less hydrogen: "The samples analyzed may have contained traces of more highly carbonized substances, and that it would be worth while to treat with $HOSO_2$ and $HONO_5$, and remove these." Beilstein and Kurbatoff met with the same difficulty in the fractions 95°–100° and 118°–120° in their attempts to ascertain the

* These Proceedings, XXVII. 78.

† Ber. der deutsch. chem. Gesellsch., 1880, p. 2028.

‡ Journ. Chem. Soc., XV. 419.

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presence in the Pennsylvania oil of the hexahydro series. The series with less hydrogen seems to be removed only very slowly, even by vigorous treatment with a mixture of nitric and sulphuric acids.

In continuing the separations above 120°, after the eleventh distillation the oils collected in considerable quantities within the limits of one degree:—

	120°–121°	121°–122°	122°–123°	123°–124°	124°–125°	125°–126°	126°–127°	127°–128°
Grams	35	40	80	70	75	75	60	40

Notwithstanding our endeavors to separate the fraction 122°–125° into higher and lower constituents, they may still be mixtures; aromatic derivatives are here present in small quantity. If in more prolonged separations distillates still persist within the same limits, they will be submitted to careful study in their behavior toward chemical reagents.

The greater portion of the fraction 125°–130° was unfortunately lost by an accident after the eleventh distillation. Sufficient however was collected at 127°–128° for a vapor density determination; it gave, by the method of Dumas, the value required for the formula C_8H_{18}; found 3.90, required 3.94. To the liquid collected by Warren at this point was assigned the boiling point 127°.6; the vapor density found by him was 3.99, and those observations seem to be confirmed by our results with the Ohio product. The portions distilling between 115° and 130° evidently need to be carefully examined in larger quantities with particular reference to the octanes. The distillates collected between 130°–145° will be considered in connection with the aromatic compounds.

Between 144° and 148°, after many distillations, the fractions were small in quantity. At the end of the sixth distillation, 65 grams collected at 149°–151°, of which 40 grams distilled constant at 149°–150°, bar. 756 mm. After prolonged heating with concentrated nitric acid a nitro-compound was formed that remained chiefly in solution in the oil. Upon dilution of the acid an oily liquid separated in small quantities. But when the oil was shaken with sodic hydrate, it became intensely red in color, and by repeated washing with the alkaline solution the nitro-product was in part removed, and it separated again as an oil by acidifying the solution. After washing, the remaining oil was dried and heated to boiling during several hours with sodium. It was then distilled from the large quantity of solid that had separated, and the greenish yellow distillate again boiled with sodium. Still more solid separated, and after distillation the oil was

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again treated with sodium until there was no further action. The boiling point was not appreciably changed by this treatment, although it was evident that some constituent had been removed capable of forming a nitro-derivative soluble in alkalies. The residual oil was shown by vapor density determinations and analysis to have the composition required for nonane. The boiling point of nonane is 150.8° (Warren).

I. 0.1799 gram of the oil gave 0.3987 gram CO_2, and 0.1749 gram H_2O.

II. 0.1751 gram of the oil gave 0.5424 gram CO_2, and 0.2488 gram H_2O.

	Calculated for C_9H_{20}.	Found. I.	Found. II.
C	84.37	84.96	84.48
H	15.63	15.16	15.88

Analysis I. was made of the oil after treatment with alcoholic mercuric chloride, but before heating with the acid mixture; analysis II. of the oil after treating with a mixture of nitric and sulphuric acids and boiling with sodium.

The determinations of vapor density of this product in the apparatus of Victor Meyer, with a bath of ethyl benzoate, gave the following results: I. 4.73; II. 4.74; required for C_9H_{20}, 4.43.

This fraction therefore contains nonane, although it consists to a very considerable extent of another hydrocarbon, which seems, by the ready formation of nitro compounds and its behavior toward alkaline solvents, to be a member of the series C_nH_{2n}. All the fractions of Ohio oil that we have examined below 150° are similarly contaminated by, or rather contain in appreciable quantities, hydrocarbons which form nitro products with the characteristic qualities of the unsaturated or paraffine nitro compounds.

Thus far Ohio petroleum has proved to contain members of the series C_nH_{2n+2}, corresponding to those which have been identified in Pennsylvania oil, but in much smaller quantities. They form one fifth of crude Pennsylvania oil and less than one tenth of Ohio oil.

In identifying these constituents it has not seemed necessary to accumulate data further than would appear essential in showing the similarity of our products to those whose composition has been so carefully demonstrated in Pennsylvania petroleum. And while this portion of our labor may be of less interest than the study of the constituents with higher boiling points, it has seemed of sufficient

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importance to justify the necessary expenditure of time and effort. The higher fractions have been quite thoroughly distilled entirely *in vacuo* to avoid decomposition so far as possible, and these products, as well as the residue above 350° of the first vacuum distillate, are reserved for later study.

Aromatic Hydrocarbons.

Series C_nH_{2n-6}.

So far as I am aware no attempts have hitherto been made to separate the aromatic hydrocarbons from the Ohio sulphur oil. In American petroleum Pelouze and Cahours found, as already mentioned, no appreciable quantities, but Schorlemmer recognized the presence of benzol and toluol. Beilstein and Kurbatoff were the first to discover the aromatic hydrocarbons in the oil from Baku, and hexahydroisoxylol in Pennsylvania petroleum.

Benzol.

After the sixth distillation of the products from the original quantity of crude oil, twenty-five grams collected at 77°–79°, 35 grams at 79°–81°, and 20 grams at 81°–83°. In each of these fractions the quantity of benzol was determined by heating carefully for some time a weighed quantity of the fraction with a mixture of nitric and sulphuric acids, distilling off the portion not affected by the acid mixture, and weighing it and the residual nitrobenzol. The fraction 77°–79° gave by this method 3 per cent of benzol; the fraction 79°–81°, 15 per cent; and the fraction 81°–83°, 5.8 per cent. The fraction 75°–76° and 85°–86°, when treated in the same manner, left scarcely any residual product after distillation, and after reduction with tin and hydrochloric acid not a trace of color was visible in applying the exceedingly delicate furfurol reaction for aniline. Calculating from these numbers, the quantity of benzol in the 41.5 kilos of crude oil taken, it amounts to 7.16 grams or 0.017 per cent, which represents approximately the quantity of benzol in the crude oil.

Toluol.

The fractions collected between 107° and 113°, after the sixth distillation under a Hempel column, were examined for toluol by treating a weighed quantity of the oil with nitric and sulphuric acids, keeping the solution cold. After some time crystals of dinitrotoluol separated, and when the hydrocarbons not affected by the acid were

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removed by distillation, there remained a heavy oil which consisted of the liquid orthonitrotoluol and crystalline dinitrotoluol. The latter soon solidified, and after crystallization from alcohol it was identified by its melting point, 71°. The loss in weight by the removal of toluol in the fraction 107°–109° amounted to 1.14 per cent, in the fraction 109°–111° to 13.07 per cent, and in the fraction 111°–113° to 2.8 per cent. The total weight of the first fraction was 50 grams, of the second 80 grams, and of the third 65 grams. These fractions, therefore, contained altogether 12.85 grams, which corresponds to 0.03 per cent of toluol in the 41.5 kilos of crude oil taken. As in the case of benzol, evidently the percentage of toluol is expressed only approximately by these results. After longer distillation the fraction 114°–115° was treated in a similar manner, but after treatment with nitric and sulphuric acids, and with tin and hydrochloric acid, the product which remained in considerable quantity after distillation did not dissolve in hydrochloric acid, and it gave no trace of color when heated with ferric chloride or with mercuric chloride. The insolubility in acids excludes in this fraction any appreciable quantity of hexahydroisoxylol which is contained in the higher portions. The oily product of the nitration must therefore be derived from another series, perhaps from an unsaturated hydrocarbon C_nH_{2n}; it will receive further attention.

Xylols.

In the first allusion to the presence of the aromatic hydrocarbons in petroleum, by De La Rue and Müller,* who found in the Rangoon oil benzol, toluol, metaxylol, and cumol, there is no evidence that the isomeric forms of xylol were discovered in that petroleum. Except paraxylol, which Pawlewski found in Galician petroleum and Engler in Pennsylvania petroleum, and metaxylol, which is generally found, it does not appear that the isomeric xylols have elsewhere been recognized in petroleum.

Between 136° and 142° in our distillates, at intervals of one degree we collected 205 grams, of which the greater portion distilled at 137°–138°, 139°–140°, and 141°–143°. After prolonged distillation these fractions collected in increased quantities at these points; they were readily acted upon by nitric acid, forming nitro compounds or oxidation products, according to the form of the reaction.

To prove the presence of paraxylol in fraction 137°–138°, a portion was treated with a mixture of nitric and sulphuric acids, at first in the

* Proc. Roy. Soc., 1856, p. 221.

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cold, then with the aid of a gentle heat. Upon distillation of the hydrocarbon not affected, there remained a brown oil that deposited a crystalline product on standing. After crystallization from alcohol, this substance appeared in the form of glistening white needles which melted at 139°–140°. It was therefore trinitroparaxylol, melting point 139°–140°.* By treating carefully another portion of the same fraction in the cold with fuming nitric acid, long yellow needles sparingly soluble in alcohol were obtained, melting at 145°, corresponding to dinitroparaxylol, melting point 147°–148°.† For further confirmation, another portion of the fraction 137°–138° was submitted to oxidation with chromic acid, and the solution extracted with a considerable quantity of ether. Evaporation of the ether left a solid residue in the form of minute prisms insoluble in water, but readily soluble in sodic hydrate. This substance sublimed without melting, and in general its properties corresponded to those of terephthalic acid. After heating for thirty hours a quantity of the same fraction with dilute nitric acid and distilling off the hydrocarbon not affected, there remained an oily product which contained no toluic acid. In repeating this experiment with longer heating, on cooling an oily layer separated above the acid, which was neutralized with sodic hydrate, evaporated to dryness, the salt decomposed with hydrochloric acid, and the solution extracted with ether. Upon evaporation a crystalline solid was left, but not in sufficient quantity for further examination; it was probably paratoluic acid.

In the fraction 139°–140° metaxylol was recognized by the formation of the trinitro-compound. A portion of the oil was heated with a mixture of nitric and sulphuric acids during forty-eight hours, the oil together with the crystals which formed was separated from the acid solution, the oil distilled, and the solid remaining with the first crystals was purified by crystallization from hot alcohol; on cooling, long slender colorless needles separated, melting at 175°–176°. This nitro compound was therefore trinitrometaxylol, melting point 176°. Several different melting points have been assigned to trinitroxylol. Luhman ‡ gave 177°, and Tilden § 182°. To explain the latter result Tilden asserted that the lower value of Luhman was due to contamination of the trinitroxylol by the isomeric nitro compounds derived

* Nölting and Geissman, Ber. der deutsch. chem. Gesellsch., XIX. 145.
† Lellmann, Ann. Chem. Pharm., CCXXVIII. 250.
‡ Ann. Chem. Pharm., CXLIV. 274.
§ Journ. Chem. Soc., XLV. 416.

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from coal tar, the source of the metaxylol from which the trinitro compound was prepared. But in the preparation of this trinitro derivative from octonaphtene, Markownikoff and Spadi * gave 179°–180° as its melting point.

An approximate quantitative determination of metaxylol was made in the fraction 139°–140° by heating a portion during one hour with dilute nitric acid, which should oxidize the para- and ortho-xylols to the corresponding toluic acids, and the remaining oil was washed with water, dried, and distilled with steam. The decrease in volume was noted, and it corresponded to 6.3 per cent of the quantity taken. The distillate was next shaken with concentrated sulphuric acid, which dissolves metaxylol, and the decrease in volume corresponded to 16.6 per cent of metaxylol. In determining the quantity of paraxylol, a weighed amount of the fraction 137°–138° was shaken thirty minutes with concentrated sulphuric acid to dissolve the ortho- and meta-xylols, with a loss in volume equivalent to 4 per cent of the quantity taken. The residual oil was then agitated with fuming sulphuric acid, and the diminished volume represented 12.2 per cent of paraxylol.

In attempting to ascertain the presence of orthoxylol, dependence was placed upon the observation of Jacobsen, that a single drop of orthoxylol may be distinguished in a mixture of the three isomers by treating them in the cold with a mixture of nitric and sulphuric acids. The fraction 142°–143° gave immediately an oily layer in considerable quantity between the acid and the lighter oil, which should be the liquid orthonitroxylol. The fraction 139°–140° gave no trace of an oily layer even after long standing. By further treatment with the acid mixture with the aid of heat, the oily mononitro product from distillate 142°–143° was converted into a crystalline dinitro compound melting at 91°, the melting point of dinitrometaxylol. By long continued action of the acid mixture, hot, a trinitroxylol was formed, nearly insoluble in alcohol, and melting at 178°, which might be a derivative either of ortho- or meta-xylol. Another portion of the distillate 142°–143° was heated with dilute nitric acid, which should form orthotoluic acid without affecting metaxylol. Upon extracting the acid solution with ether, an oily residue remained after evaporation of the ether with the characteristic odor of toluic acid, but no crystals separated even after long standing. An attempt was made to separate the less soluble sodic orthoxylol sulphonate, but upon evaporation of

* Ber. der deutsch. chem. Gesellsch., 1887, p. 1850.

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the solution no crystalline product appeared until the solution was so far concentrated that the sodic metaxylol sulphonate was deposited. Orthoxylol cannot therefore be present in any appreciable quantity.

Determinations of the constituents capable of forming nitro products were also made in the fractions containing the xylols by treatment with a mixture of nitric and suphuric acids according to the method employed for benzol and toluol. The quantity of xylol corresponding to the nitro product represented by the portion not affected by nitric acid in the fraction 137°–138° was 54.3 per cent of the weight of oil taken; in the fraction 139°–140°, 72.1 per cent; and in fraction 141°–143°, 31.5 per cent. Calculating the percentages of xylols from the results of the first determination in the 41.5 kilos of crude oil first distilled, the quantity of metaxylol is 0.016 per cent, and of paraxylol, 0.013 per cent. Evidently the xylols were not wholly collected in their respective fractions, although the quantity outside of the limits, 137°–143° was doubtless small. Probably at least one third should be added to these results. But if the percentages were increased to the results obtained by the action of concentrated nitric acid, the quantities of the xylols in the crude oil would still be small. In the fractions 132°–136° we observed the presence of aromatic hydrocarbons, although in too small amounts for identification; nitro products were formed by the action of nitric acid. Attempts were made to ascertain the presence of ethylbenzol and hexahydromesitylene, but without success, on account of the limited quantity of the distillates. After treatment of the fraction 135°–136° with concentrated nitric acid to convert the hydrocarbons C_nH_{2n-6} into nitro products, and distilling off the hydrocarbons not affected by the acid, the distillate was heated for some time with a mixture of nitric and sulphuric acids. According to Baever,* fuming nitric acid readily converts hexahydromesitylene into trinitromesitylene; but Konowaloff † found that a mixture of nitric and sulphuric acids, or fuming nitric acid, forms the trinitro compound only very slowly. After prolonged heating we obtained a crystalline nitro compound, but in such small quantity that it was impossible further to identify it. A much larger supply of these distillates will be necessary to determine the presence of these bodies.

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* Ann. Chem. Pharm., CLV. 275.

† Ber. der deutsch. chem. Gesellsch., 1887, p. 1850.

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Series C_nH_{2n}.

Hexahydro compounds (Beilstein and Kurbatoff); naphtenes (Markownikoff and Ogloblin).

The lower members of this series include: —

Hexahydrobenzol, C_6H_{12},	boiling point, 69°.
Hexahydrotoluol, C_7H_{14},	boiling point, 97°.
Hexahydrocumol, C_9H_{18},	boiling point, 147°–150°.
Hexahydrocymol, $C_{10}H_{20}$,	boiling point, 171°–173°.
Hexahydroisoxylol, C_8H_{16},	boiling point, 118°.
Hexahydromesitylene, C_9H_{18},	boiling point, 135°–138°.

In examining Ohio petroleum for the lower hydrocarbons of this series, the fraction 69°–70°, after the fourteenth distillation, was shaken with concentrated nitric acid, then with concentrated sulphuric acid, and finally heated with metallic sodium. Determinations of carbon and hydrogen in the purified oil gave results corresponding to the composition of hexane: —

I. 0.1618 gram of the oil gave 0.4934 gram CO_2, and 0.2299 gram H_2O.

II. 0.1891 gram of the oil gave 0.5790 gram CO_2, and 0.2663 gram H_2O.

	Required for		Found.	
	C_6H_{14}.	C_6H_{12}.	I.	II.
C	83.72	85.71	83.18	83.51
H	16.28	14.28	15.79	15.65

Hexahydrobenzol is therefore not present in appreciable quantities in Ohio petroleum.*

The fraction 96°–97°, bar. 750 mm., after the fourteenth distillation, was purified as before, and the composition determined by analysis: —

* Recently Markownikoff (Ber. der deutsch. chem. Gesellsch., 1895, p. 577) has ascertained that hexanaphten (hexahydrobenzol) which he formerly reported as a constituent of Caucasus naphtha, boiling at 69°–71°, is not a single body. Since the discovery by Baeyer of hexamethylen, boiling point 79°, Markownikoff has discovered that Caucasus naphtha contains rather this same hexamethylen which he has identified by the formation of its nitro products. It will, therefore, be necessary to examine more carefully the corresponding distillates from the oils we have under examination for this body.

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I. 0.2083 gram of the oil gave 0.6423 gram CO_2, and 0.2849 gram H_2O.

II. 0.2010 gram of the oil gave 0.6200 gram CO_2, and 0.2744 gram H_2O.

	Required for C_7H_{13}.	Required for C_7H_{14}.	Found. I.	Found. II.
C	84.00	85.71	84.09	84.72
H	16.00	14.28	15.27	15.17

This oil was evidently heptane contaminated, as shown by the low percentage of hydrogen, by a hydrocarbon containing less hydrogen. To remove any doubt as to the presence of heptane, the oil was heated during fifteen hours with a mixture of nitric and sulphuric acids, the oil separated from the acid, washed, dried, and boiled for some time with sodium. It was then distilled from the large amount of colored residue, again boiled with sodium, and distilled. The last distillation left very little residue, and the distillate was nearly odorless. The residue from the treatment with sodium crystallized well from alcohol. Upon diluting the acid a heavy nitro product separated in considerable quantities. A combustion of the purified oil gave the following percentages of carbon and hydrogen: —

0.1410 gram of the oil gave 0.4224 gram of CO_2, and 0.2065 gram H_2O.

	Required for C_7H_{16}.	Found.
C	84.00	83.75
H	16.00	16.28

In a distillate 95°–100° from American ligroine, Beilstein and Kurbatoff* found 84.8 per cent of carbon and 15.4 per cent of hydrogen. After prolonged heating with nitric acid, the oil distilled at 98°.5 – 99°.5, and gave on analysis 84.2 per cent of carbon and 15.9 per cent of hydrogen, from which it was inferred that hydrocarbons poorer in hydrogen were contained in the crude ligroine. A nitro derivative was separated from this fraction with the composition of nitropropane, $C_7H_{15}NO_2$. The fraction from Ohio petroleum gave no nitro compound when treated with nitric acid, and the acid was diluted.

Scarcely any residue remained when the oil was distilled after the treatment with acid. With a mixture of nitric and sulphuric acids, as shown above, much nitro compound separated upon dilution, which was

* Ber. der deutsch. chem. Gesellsch., 1880, p. 2028.

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soluble in potassic hydrate like the nitro derivatives of the series C_nH_{2n+2}, and by boiling with sodium the solid residue was large.

In distillates 85°–105° from Bibi-Eibat and from Balakhani, after thirty fractional separations, Milkowsky * collected a body that distilled constant at 100°–101°, and by the formation of its halogen derivatives proved it to be heptanaphtene. The oil boiling at 101°–103°, which Beilstein and Kurbatoff separated from Baku oil, was doubtless the same product, but Beilstein and Kurbatoff considered it to be composed for the most part of hexahydrotoluol, boiling point 97°.

Hexahydroisoxylol was found by Beilstein and Kurbatoff in Caucasus petroleum,† and in American ligroine;‡ since the American source was not mentioned, it is to be inferred that the ligroine was prepared from Pennsylvania oil. In testing the fractions 118°–119°, fourteenth distillation in a Hempel column, for hexaisoxylol, a portion of the oil was heated forty hours with a mixture of nitric and sulphuric acids. The nitro product separated from the oil when cold in long, flat plates, nearly insoluble in cold, more readily in hot alcohol. When purified by crystallization, this substance melted at 177°, and was, therefore, trinitroisoxylol. A similar crystalline nitro product with the same melting point was found in the fraction 123°–124°. Since the prolonged distillation precluded the possibility that this fraction contained metaxylol, there can be no doubt that the trinitroxylol obtained from fraction 118°–119° indicated the presence of hexahydroisoxylol, although it evidently formed only a small proportion of this product. After a portion of the same distillate was agitated thoroughly with a mixture of nitric and sulphuric acids, and distilled over sodium, analysis gave the percentages of carbon and hydrogen required for octane, as has been shown (page 30): —

	Required for		Found.		
	C_8H_{18}.	C_9H_{18}.	I.	II.	III.
C	84.20	85.71	84.42	84.28	84.20
H	15.79	14.28	15.19	15.08	16.10

As already explained, Analysis III. was made after prolonged treatment with the mixture of acids by which the hexahydro compound is removed very slowly, and the final results show that the fraction is composed chiefly of the more highly hydrogenized hydrocarbon, although it contains a considerable quantity of the other constituent, as shown by the abundant formation of nitro product.

* Ber. der deutsch. chem. Gesellsch., 1885, c. 187.

† Ibid., 1880, p. 1818. ‡ Ibid., p. 2088.

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In the intermediary product from the separation of octonaphtene and nononaphtene, by prolonged boiling with sodium and treatment with fuming sulphuric acid, Putochin * obtained a hydrocarbon distilling at 122°–124°, principally at 122°.5, which corresponded in its composition to the formula C_8H_{18}. It gave a chloride different from the corresponding derivative of octonaphtene, and it was therefore accepted as isooctonaphtene. By treatment of the chloride with alcoholic potassic hydrate, isooctonaphtylene was formed with a higher boiling point than naphtylene from octonaphtene.

The principal features of the Ohio sulphur petroleum which have appeared in the course of this examination are the following.

1. The crude oil is heavier than the Pennsylvania, and lighter than the Russian oil. In the quantities of the higher distillates, and in its general properties it resembles more nearly the latter.

2. It differs from other petroleums in the large amounts of sulphur compounds which exert an influence on the general properties of the oil.

3. It resembles the Pennsylvania oil in containing below 150° members of the series C_nH_{2n+2}, although in much smaller quantities. The presence in the Ohio oil of the two isomeric series C_nH_{2n+2} confirm the observations of Warren on the Pennsylvania petroleum.

4. The aromatic hydrocarbons are here present in minute quantities, apparently much smaller than in other petroleums. Benzol, toluol, meta- and para-xylol have been identified. The hexahydro series C_nH_{2n} is represented by hexahydroisoxylol, and very probably by higher members, although this has yet to be determined. Hexahydrobenzol and hexahydrotoluol are not contained in this petroleum.

5. By the formation of characteristic nitro products, and the results of bromine absorption, the presence in the crude oil of unsaturated hydrocarbons C_nH_{2n} seems to be indicated.

Portions of Ohio petroleum have been thoroughly fractioned, and are now under examination to establish the identity of the octanes, to ascertain whether isooctonaphtene and hexahydromesitylene are present, and to ascertain whether this petroleum contains α-nonane, boiling point 135°–137°, and β-nonane, boiling point 129°.5–131°.5, which Lemoine † asserts is contained in Pennsylvania petroleum. Examination of distillates collected above 150° is now in progress.

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* Ber. der deutsch. chem. Gesellsch., 1885, p. 186.

† Bull. Soc. Chim., 1884, XLI. 164.

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Canadian Petroleum.

Closely connected with the chemistry of Canadian petroleum are certain features relating to its occurrence, and the associated geological formations, which have not been fully investigated. The deposits of petroleum in Canada have been longer known than those in the Lima and Findlay fields in Ohio. As early as 1857 the existence of oil in considerable quantity in the township of Enniskillen was ascertained, and in 1862, the first flowing well was started. It was estimated by Dr. Winchell * that during the summer of 1862 not less than 5,000,000 barrels of oil flowed off on the waters of Black Creek. The flow of these early wells was very large. At a depth of 188 feet as much as 6,000 barrels of oil daily escaped from a single well, and at 237 feet 7,500 barrels daily, nearly equal to the flow of the great wells at Baku.

It is now known that these deposits of oil were mainly in the form of "pockets," and they formed no part of the main fields which are still productive. This oil territory is situated on two parallel anticlinals, about ten miles apart, with the corresponding synclinal between, from which no oil is obtained. In various reports of these oil fields, the larger area of oil-bearing strata at Petrolia is given as twenty-seven square miles, but the really productive field is actually contained within an area of less than eight square miles. The productive field at Oil Springs is included within an area of less than two square miles. The oil deposits are here found in the Corniferous limestone underlying the Hamilton group of shales and limestones. Unlike the Trenton oil rock in Ohio, the oil-bearing limestone is quite near the surface; the usual depths of wells at present in the Petrolia field is 465 feet.

I am indebted to the experience and extended observations of Messrs. M. G. Woodward of Petrolia and F. J. Carman for valuable information concerning the geological features and technology of the Canadian oil, of which a more detailed account will elsewhere be given.†

Under the general title of American petroleum, with occasional reference to Pennsylvania and to Canada as the particular sources, several partial examinations of crude Canadian oil were early made by French and English chemists. The first examination of Canadian

* Geological Report of Canada, 1888–89.

† A paper soon to be presented at the Franklin Institute.

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oil was undertaken by Pelouze and Cahours * for the purpose of separating and identifying the hydrocarbons therein contained. Their attention was confined to the series C_nH_{2n+2}, and published accounts of their work contain no allusion to any other constituents than this series of hydrocarbons. They failed to observe the presence of aromatic hydrocarbons, although, as already mentioned, Schorlemmer discovered the presence of the benzol hydrocarbons in "real Canadian rock oil, a thick black liquid of a very unpleasant odor."

My attention was first attracted to Canadian petroleum in 1890, when I procured some of the crude oil and also a quantity of the "sludge" from the refining of burning oil, for the purpose of examining the sulphur compounds. The peculiar features of the distillates in a preliminary examination † invited further attention, and I determined to undertake, with the aid of the refiners, as complete an examination as was possible with the appliances at my command. It may seem somewhat surprising that such an examination of the sulphur petroleums in general has not previously been undertaken; but it should be borne in mind that it requires the facilities of a well equipped organic and technological laboratory for the manipulation of considerable quantities of material, and a corps of efficient chemists with aid from the refinery of crude oils, partially refined products, and residues. Even with all necessary accessories, aside from the tedious routine labor, there are certain features of decomposition and slow separation of constituents that render this work extremely difficult. In view of possible changes in the composition of petroleum, in the course of time, as wells become exhausted or the oil is taken from different depths, or indeed with the possibility of future exhaustion of oil fields which at present appear to be in the zenith of their production, it would seem that a comprehensive study of these oils should not be too long delayed.

From the peculiar nature of petroleum and its numerous constituents, all of which, so far as they have been examined aside from the lighter hydrocarbons of the series C_nH_{2n+2}, or the series C_nH_{2n}, are present in small quantities, any attempt toward a separation of these constituents involves the manipulation of large volumes of the oils in such a manner as to prevent so far as possible decompositions, which cannot be entirely avoided even with the greatest care. On this account satisfactory results can be hoped for only in products that have

* Bull. Soc. Chim., 1863, p. 228.

† Amer. Chem. Journ., 1894, p. 89.

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been obtained, at least in part, in experiments with several hundred barrels of oil, which must be performed with the aid of the appliances in a refinery. On the other hand, an examination of the unstable sulphur oils for certain constituents can be carried on satisfactorily only on a smaller scale, with laboratory appliances.

The products which I obtained through the aid of Messrs. Samuel Rogers & Co., of Toronto, and Mr. J. H. Fairbanks, of Petrolia, for the study of Canadian petroleum, included a barrel of crude oil, considerable quantities of the first distillate, naphtha distillate, and burning oil distillate, none of which had been further refined, besides 200 litres of thoroughly washed sulphur oil from "sludge." The crude oil was thick and nearly black in color; it contained hydric sulphide in small quantity, and some water, which was removed only after long standing in intimate contact with fused calcic chloride, and even then a small quantity appeared in the first distillate. A determination of its specific gravity at 20° gave 0.8621. In a former determination in another quantity of the crude oil we reported 0.8600.* Determinations in other specimens gave the following results: —

Oil Springs		0.8442
"		0.8427
"	(gas oil)	0.8389
Petrolia		0.8553

These numbers are not essentially different from those reported in other examinations of these oils. H. P. Brummel † gave as the specific gravity of the Canadian oils 0.804 and 0.808, values which must be accepted as only approximate, rather than as results of accurate determinations. Markownikoff and Ogloblin ‡ referred to results of Sainte Claire Deville, which gave 0.844 as the specific gravity of Canadian oil, and 0.887 for Ohio oil. Reference to the original publication of Deville § shows that he obtained 0.870 as the specific gravity of Petrolia oil, and 0.844 for oil from "Canada West" (Oil Springs?). The numbers assigned by Redwood ‖ to the oils at Petrolia were 0.859–0.877, and to the oils from Oil Springs 0.844–0.854. As Engler observed in the Alsace oils, it is possible that the specific gravity diminishes with the depth of the well.

* Amer. Chem. Journ., 1894, p. 90.
† Canadian Geological Report, 1888–89.
‡ Ann. Chim. Phys., [6.], II. 372.
§ Comptes Rendus, LXVIII. 485.
‖ Journ. Soc. Chem. Ind., 1887, p. 405.

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Determinations of sulphur in the crude oil gave the following percentages: —

	I.	II.	III.	Oil Springs.
Sulphur	0.98	0.99	1.06	0.60

Canadian petroleum contains somewhat less carbon and hydrogen than Ohio oils: —

I. 0.1908 gram of Petrolia oil gave 0.5874 gram of CO_2 and 0.2295 gram H_2O.

II. 0.1914 gram of Oil Springs oil gave 0.5868 gram CO_2 and 0.2305 gram H_2O.

	I.	II.
C	83.94	83.62
H	13.37	13.39

In the Canadian Geological Report above mentioned Brummel gave 85 per cent for carbon and 15 per cent for hydrogen. These percentages are evidently only approximate. They do not agree with results earlier obtained by Pelouze and Cahours, who reported a considerable percentage of oxygen.*

C.	H.	O.
84.2	13.4	3.0

The variation in composition in the Canadian, Ohio, Pennsylvania, and Russian petroleums is shown in the following table: —

	Canadian.	Ohio.	Pennsylvania.	Russian.
C	83.94	84.57	84.19	86.89
H	13.37	13.62	13.70	13.18

After accounting for one per cent of sulphur in the Canadian oil and 0.70 per cent in the Ohio oil, the remaining percentage may reasonably be assigned to oxygen, yet in the Russian oils the composition is fully accounted for by the carbon and hydrogen, although the presence of oxygen compounds in considerable quantity has been demonstrated in several independent investigations.

Having an opportunity to collect fragments of the oil rock at Petrolia soon after it had been removed in drilling a well, I have ascertained its composition. Like most wells in this territory, the oil-bearing stratum was reached at a depth of 465 feet. The driller distinguishes two varieties of rock, one stratified and offering less resistance

* *Loc. cit.*

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to the drill than the other, which is finer grained and for the most part loose and granular like sand. For convenience these specimens may be designated as I. and II. consecutively, and their composition is shown by the following results of analysis, to which is appended for comparison the composition of the Trenton limestone at Findlay, III., at a depth of 1,096 feet, and of the same oil rock at Lima, IV., at a depth of 1,247 feet.*

	I.	II.	III.	IV.
Calcic carbonate	49.80	49.75	53.50	52.66
Magnesic carbonate	44.35	45.44	43.05	37.53
Silicious residue	0.52	0.80	1.70	4.15
Alumina and iron	0.46	1.00	1.25	

It therefore appears that the dolomitic condition is not wanting in the oil-bearing Corniferous limestone; in fact, magnesic carbonate seems to be somewhat in excess of the quantity present in the Ohio Trenton limestone. The specimens were impregnated with oil and were thoroughly washed with gasoline to remove so far as possible the carbonaceous portion.

In a distillation of Petrolia oil under atmospheric pressure, the first distillate appeared at 115°, and the following weights in grams were obtained from 800 grams: —

	115°-150°	150°-200°	200°-250°	250°-300°	300°-350°	Residue.	Loss.
Weights	22	62.5	72	43	27	561	12
Per cent	2.75	7.8	9.5	5.1	3.1	70.1	1.75
Sp. Gr.	0.767	0.8026	0.8228	0.8345	0.9037		

In the proportions that distil at different temperatures and in the specific gravity of the distillates, the Oil Springs resembles more nearly the Findlay oil: —

	— 100°	100°-150°	150°-200°	200°-250°	250°-300°	300°-350°	Residue.	Loss.
Weights	8	41	90	62	88	47	357	7
Per cent	1.14	5.86	12.85	8.86	12.6	6.71	51.0	0.98
Sp. Gr.		0.7335	0.7675	0.7984	0.8222	0.8386	0.9032	

A comparison of the distillates at increasing temperatures from oils of different localities has been included in considering the properties of the Ohio oils. A clearer idea of the peculiar character of Canadian oil may be gained by comparing the distillates from it with

* Orton, Geological Survey of Ohio, 1890, p. 13.

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those from oils of other fields. It is evident that the high specific gravity of the Canadian and Ohio crude oils depends upon constituents that do not distil below 350°. In this respect these oils differ essentially from the Russian oil, in which all the distillates show a high specific gravity. The distillates below 150° from Canadian oil are somewhat lighter than the corresponding products from Ohio crude oil. In considering later the properties of the vacuum distillates it will be seen that these proportions are very materially changed by distillation *in vacuo*.

	Apscheron.		Pennsylvania.	
	Per cent.	Specific Gravity.	Per cent.	Specific Gravity.
120°–150 °	0.5		19.70	
150°–200°	10.9	0.786	8.85	0.757
200°–250°	12.8	0.824	15.23	0.788
250°–320°	24.7	0.861	20.70	0.809
	48.9		64.48	
Residue	51.1		35.52	

Canada.

	Petrolia.		Oil Springs.	
	Per cent.	Specific Gravity.	Per cent.	Specific Gravity.
— 100°			1.14	
100°–150°	2.75	0.7670	5.86	0.7335
150°–200°	7.80	0.8026	12.85	0.7675
200°–250°	9.50	0.8228	8.86	0.7984
250°–300°	5.10	0.8345	12.60	0.8222
300°–350°	3.10	0.9037	6.71	0.8386
	28.25		48.02	
Residue	70.10		51.00	

	Ohio.	
	Per cent.	Specific Gravity.
110°–150°	9.75	0.7282
150°–220°	16.63	0.7669
220°–257°	10.75	0.7940
257°–300°	9.75	0.8138
300°–350°	8.63	0.8242
	55.51	
Residue	43.00	

In the percentages of the lower fractions it will be seen that the Canadian oil resembles more nearly that from the Caucasus, but the

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residue above 350° is much larger than in the oils from other fields. As will appear later, this difference is much less in distillations conducted *in vacuo*.

The percentage of sulphur was determined in each distillate by a combustion in air: —

	115°–150°	150°–200°	200°–250°	250°–300°	300°–350	Residue.
Sulphur	0.28	0.42	0.50	0.51	0.86	0.70

Determinations of the quantity of bromine absorbed indicated a greater capacity for absorption in the higher fractions, but less in the residue than in corresponding fractions from the Ohio oil: —

Canada.		Ohio.	
Fraction.	Per cent of Bromine.	Fraction.	Per cent of Bromine.
115°–150°	0.67	110°–150°	0.73
150°–200°	1.12	150°–220°	1.74
200°–250°	3.49	220°–257°	4.84
250°–300°	8.39	257°–300°	5.04
300°–350°	14.4	300°–330°	12.10
+ 350°	17.8	+ 330°	19.50

The Oil Springs oil differs essentially in many respects from Petrolia oil, especially in its lower specific gravity, lower percentage of sulphur, and in the proportions in which it distils at different temperatures. In certain peculiarities it approaches Ohio oil. The lower fractions show a higher bromine absorption than either the Petrolia or the Ohio oil: —

	Per cent of Bromine absorbed.
—100°	0.0
100°–150°	2.31
150°–200°	4.09
200°–250°	8.98
250°–300°	8.41
300°–350°	12.00
+ 350°	33.78

The percentage of bromine absorbed by the crude oils was also determined: —

Petrolia.	Oil Springs.	Ohio.
15.11	17.69	10.19

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Hydric sulphide escaped in small quantities during the distillation, but below 200° the decomposition was slight, and the distillates were colorless. Above this point the products were somewhat colored, with the disagreeable odor of decomposition. It is probable that cracking begins near this temperature, affecting the unsaturated hydrocarbons if they are present, and perhaps other series as well as the sulphur compounds. Certain constituents of the Canada oil seemed to be more unstable than those of Ohio petroleum. The tendency toward polymerization of unsaturated hydrocarbons separated from distillates corresponding to burning oil has been observed by me.* An oil that had been distilled many times *in vacuo* and allowed to stand two years, when again heated suddenly polymerised into a higher product that could not be distilled at any temperature on account of complete decomposition. The conversion of Canadian petroleum into asphalt, upon long standing exposed to the weather, is well known. Large masses of this material may be seen in a pitchy form in the vicinity of Oil Springs.

Determinations of carbon and hydrogen were made in the coke from Petrolia oil, in one sample from the crude oil, and in another from a tar distillate with the following results: —

	Crude Oil.	Tar Distillate.
C	94.04	94.34
H	4.19	4.34

A specimen of "surface" oil was collected at Oil Springs for examination. It was very thick, with the consistency of ordinary molasses. A determination of its specific gravity at 20° gave 0.9059. It contained 0.05 per cent of nitrogen, and 0.95 per cent of sulphur. The weight of bromine absorbed was equivalent to 25.46 per cent. This oil is evidently an intermediary product in the formation of the deposits of pitch resembling asphalt, which have long been known at Oil Springs. The pitch is evidently formed by evaporation from the oil of the more volatile constituents, and its formation is doubtless due, in part at least, to polymerization of lower constituents of less stability. A combustion of this pitch gave 64.86 per cent of carbon and 8.13 per cent of hydrogen. In a determination of nitrogen 0.40 per cent was obtained, and the percentage of sulphur was found to be 0.65. The pitch contained 10.13 per cent of ash, and a qualitative examination showed that it was composed chiefly of calcic oxide, with smaller

* Amer. Chem. Journ., 1894, p. 92.

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amounts of aluminic and ferric oxides, besides a trace of magnesic oxide. A determination of its bromine absorption gave 37.79 per cent.

Nitrogen was determined in each variety of coke, and in several samples of crude oil by the Kjeldahl method : —

Coke from crude oil	0.38
Coke from tar distillate	0.31
Petrolia crude	0.16
Oil Springs	0.18
Oil Springs gas oil	0.21

Sulphur was determined in the two varieties of coke, and in a specimen of crude paraffine wax :—

Coke from crude oil	0.76
Coke from tar distillate	0.76
Crude paraffine wax	0.97

When it is remembered that this coke in the process of carbonization had been exposed to a temperature closely approaching a red heat, it is not easy to understand how it could retain so large a proportion of nitrogen and sulphur. If the ash was sufficient in quantity, the presence of metallic cyanides and sulphides might be assumed. But 0.07 per cent of ash is not sufficient to account for such a high percentage of sulphur. Moreover, careful tests failed to show the presence of either sulphides or cyanides. In determinations of sulphur by combustion in air, we have frequently found that the carbon must be completely burned, otherwise the percentage of sulphur is too low.

With the purpose of ascertaining the mineral constituents of Canadian petroleum I procured a specimen of coke from the distillation of the crude oil, and another from the coking of a tar distillate. Since finely divided mineral matter is frequently held in suspension in the crude oil long after it is taken from the well, it might be inferred that the ash from the crude oil should consist in part of suspended material. The specimen selected was a part of a large fragment, one side of which had evidently been carbonized in contact with the bottom of the still. The portion for analysis was taken from the opposite side, which had evidently been carbonized several inches above the bottom. The residue from combustion in oxygen corresponded in the crude oil coke to 0.17 per cent, and in the coke from the tar distillate to 0.07 per cent. These quantities of ash correspond to 0.012 per cent in the crude oil. An examination of the ash showed that it was composed of

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the oxides of magnesium, calcium, iron, and aluminum. It consisted chiefly of the oxides of calcium and magnesium, doubtless derived from the dolomitic reservoir.

A quantity of brine was collected for examination at Petrolia from a well recently drilled. Analysis showed that it contained calcic sulphate, and calcic, magnesic, and sodic chlorides, in the following proportions in 1,000 parts: —

NaCl	10.71
$MgCl_2$	2.90
$CaCl_2$	1.20
$CaSO_4$	3.20
Iron and alumina	traces.
	18.00

The specific gravity of this brine at 20° was 1.0165.

The composition of this brine is quite different from that given in the early history of this oil territory by Dr. T. Sterry Hunt. We made no examination for potassic chloride. 1,000 parts of the brine gave in Hunt's analysis: —

NaCl	4.800
KCl	0.792
$CaCl_2$	12.420
$MgCl_2$	3.650
	21.662

It is practically impossible, at least in glass, to distil the Canadian oil on a small scale unless it is free from water, and the water can be removed only by long standing with large quantities of calcic chloride.

After the first distillation there is less difficulty in removing water except in the least volatile distillates. The necessity of vacuum distillation to avoid decomposition was even more evident in Canadian than in Ohio oil. In quantities of 12 litres each, 64.5 kilos were distilled in a porcelain still under a tension of 50 millimeters, and the following quantities of the distillates were collected at different temperatures: —

	— 100°	100°–150°	150°–200°	200°–250°	250°–300°	300°–350°	Residue
Grams	3870	7288	7159	8578	7869	6698	22059
Per cent	6.00	11.3	11.1	13.3	12.2	10.4	34.2
Per cent in Ohio oil	18.6	19.8	15.1	18.0	250°–350° 6.2		20.9
Sp. Gr.	0.7549	0.7852	0.8161	0.8387	0.8647	0.8759	0.9189
Sp. Gr. of Ohio oil	0.7445	0.7941	0.8245	0.8455	0.9070		0.913

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It is peculiar that in distillation under atmospheric pressure as well as *in vacuo* the lowest fraction from the Canadian oil is heavier than that from Ohio oil, while the next following distillates are reversed in the order of their specific gravity. Under the influence of vacuum distillation a large portion of the heavier constituents of the residue above 350°, under atmospheric pressure, are reduced in boiling points to such an extent that the specific gravity of the lower fractions is very considerably increased. Referring to the specific gravity of the fractions from the Apscheron oil, page 48, it will be seen that the corresponding fractions *in vacuo* from the Canadian oil are much heavier, and the residue is much smaller. The differences between the weights collected at different temperatures in the Canadian and Ohio petroleum also confirm the marked variation in composition already referred to, and an explanation must evidently be sought in the larger quantities of the series C_nH_{2n+2} in the fractions below 150° from Ohio oil, and the greater quantity of the heavier oils of the series C_nH_{2n} and similar series in distillates from Canadian oil above this point.

The percentages of sulphur in these distillates were also determined:

	—100°	100°–150°	150°–200°	200°–250°	250°–300°	300°–350°	Residue.
Sulphur	0.25	0.45	0.47	0.75	0.78	0.81	0.83

When distilled without much decomposition the sulphur compounds in Canadian oil collect in smaller quantities in the lower distillates than is the case in Ohio oil.

Determinations were made of the per cent of bromine absorbed by the vacuum distillates: —

	100°	100°–150°	150°–200°	200°–250°	250°–300°	300°–350°	Residue.
Bromine abs.	0	3.25	4.59	6.2	8.2	15.8	25.82
Bromine abs. atm. pressure		0.67	1.12	3.49	8.39	14.4	17.8
Br. abs. Ohio oil, vac. dist.	0	4.57	6.60	250°–350° 7.08			24.38

There is a marked difference in bromine absorption between the distillates collected *in vacuo* and those collected under atmospheric pressure. The capacity for absorbing bromine in the distillates from Canadian oil is greatly increased in the lower fractions by vacuum distillation, and this difference is even more noticeable in Ohio oil. It is probably due to the smaller amounts of Canadian oil distilling at lower temperatures under atmospheric pressure. The larger quanti-

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ties of bromine absorbed in the fractions collected *in vacuo* is suggestive. It cannot be caused by decomposition, but it seems to be due rather to the reduction in boiling points by which certain compounds capable of absorbing bromine are carried over at lower temperatures, and doubtless too with less decomposition. The increased absorption above 250° may indicate cracking, or the presence of normal constituents that absorb bromine. Since the difference in the amounts absorbed in the Canadian oil *in vacuo* and under atmospheric pressure is not large except in the residues, and the conditions much less favorable for cracking in the vacuum distillates, it would seem that the absorptive capacity is due to normal constituents of the crude oil.

The fraction 150°–200°, containing 0.47 per cent of sulphur, absorbed 4.59 per cent of bromine. A portion was treated with alcoholic mercuric chloride, washed, dried, and it was then found to contain 0.063 per cent of sulphur. A determination of the amount of bromine it absorbed gave 2.8 per cent. This result is evidently independent of the sulphur compounds. It must indicate either normal constituents of the oil with an affinity for bromine, or the presence of decomposition products due to cracking.

Another portion of the same fraction was agitated with concentrated sulphuric acid, and the quantity of bromine then absorbed was equivalent to 1.15. Since mercuric chloride has been shown to remove nearly all the sulphur compounds from the lower fractions, and sulphuric acid only partially, it is still further evident that there are present in this fraction other bodies capable of absorbing bromine, perhaps unsaturated hydrocarbons, either contained in the crude oil or resulting from decomposition during distillation.

The distillates collected *in vacuo* showed but slight indications of decomposition; they were only slightly discolored, except the residue above 350°. In prolonged distillation the higher fractions gradually become colored by polymerization or other decomposition. Even the residue above 350° showed scarcely any odor, and it had apparently undergone but little decomposition. The distillates above 150° and the residue above 350° are reserved for further study.

As in the study of Ohio petroleum, the lower members of the series C_nH_{2n+2} were sought for in the most volatile refinery distillate. Twenty litres of the very first distillate from Petrolia crude oil was submitted to distillation, and the vapors collected in a Warren condenser filled with a freezing mixture or with water, according to the boiling points of the distillates, and with a condensing worm in front filled with the freezing mixture. Distillates were collected below 45°, and the dis-

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tillation of them repeated until they collected for the most part within well defined limits. The following weights were collected as representing the quantities of these products in the twenty litres first distilled: —

—10°	10°-20°	20°-25°	28°-30°	30°-35°	36°-38°
100	40	30	175	30	80

The small quantities distilling at temperatures outside of the boiling points of the well known hydrocarbons were not further examined, since it was assumed that they were merely mixtures. The portion collecting at 29°–30° in a vapor density determination gave 2.54; required for is opentane 2.49.

A vapor density determination of the fraction 36°–37° gave 2.66, which corresponds to the composition of pentane, C_5H_{12}.

Distillation of the portion —10° was continued until 20 grams collected between 7° and 8°. In a vapor density determination by the method of Hofmann, the value 2.01 was obtained; calculated for butane, C_4H_{10}, 2.01. A considerable portion of this oil collected below 5°; which consisted chiefly doubtless of the butane that boils at 0°. But since this body has been identified no further attempts were made to separate it more completely. Concerning the butane boiling at 8°, what has been said of the same product separated from Ohio petroleum applies also here. It is evident from the weights collected of these volatile hydrocarbons that they are present in much smaller quantities than in Ohio petroleum.

The distillate below 150° *in vacuo* was fractioned twelve times, collecting at first within 5° limits, then within 2°, and finally within 1°, with the aid of Warren condensers containing glass coils and Hempel columns. At the end of the eighth distillation, the last seven under atmospheric pressure, the lower distillates collected as follows, with smaller quantities between these limits: —

	—55°	55°-60°	65°-69°	77°-83°
Grams	8	25	40	65

As was mentioned when considering the lower fractions of the Ohio oil, these weights evidently represent only approximately the quantities in the crude oil.

After the eighth distillation, the fractions 55°–60° were further purified, until 15 grams distilled constant at 60°–61°, bar. 749 mm., and a vapor density determination of this product gave 2.96; required for isohexane, 2.98.

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At 67°–68°, after the twelfth distillation, 10 grams of oil collected, which gave as its vapor density 3.01; required for hexane, 2.98. The distillates 75°–85° will be considered with the aromatic series.

At 87°–93°, after the eighth distillation, the distillates amounted to 115 grams, and after the fifteenth, 20 grams distilled at 90°–91°, bar. 745 mm. A vapor density determination of this product gave 3.51; isoheptane, C_7H_{14}, requires 3.46.

At the end of the seventeenth distillation, 80 grams collected at 96°.5 – 97°.5, bar. 740 mm., which distilled constant within these limits. A determination of its vapor density gave 3.63; required for heptane, 3.46. The composition of this oil was further established by analysis: —

0.1870 gram of the oil gave 0.5781 gram CO_2, and 0.2514 gram H_2O.

	Required for C_7H_{16}.	Found.
C	84.00	84.31
H	16.00	15.77

Outside of the limits of temperature within which the hydrocarbons C_nH_{2n+2} have been found, the distillates below 105° have been subjected to prolonged distillation, but the quantities collected were so irregular, gradually separating into higher and lower constituents, that it excluded the presence in any considerable quantity of other bodies. The fractions in the vicinity of 111° will be described later, in the examination for toluol.

Concerning the distillates collected at 118°–119°, the observations on the corresponding fractions from Ohio oil apply equally here. At 118°–119°.5, the distillates amounted to 90 grams after the fifteenth distillation. A vapor density determination gave 4.02; required for octane, C_8H_{16}, 3.94. As in the case of the Ohio products, this fraction was purified with much care, and the following determinations of carbon and hydrogen were made: —

I. 0.2013 gram of the oil gave 0.6226 gram CO_2 and 0.2738 gram H_2O.

II. 0.2036 gram of the oil gave 0.6318 gram CO_2 and 0.2799 gram H_2O.

III. 0.2045 gram of the oil gave 0.6324 gram CO_2 and 0.2762 gram H_2O.

	Required for C_8H_{18}.	Found.		
		I.	II.	III.
C	84.20	84.35	84.61	84.33
H	15.79	15.12	15.28	15.01

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From the low percentage of hydrogen and higher percentage of carbon it was evident that this oil still contained a small amount of a hydrocarbon with less hydrogen, probably of the series C_nH_{2n}, although the main constituent was evidently a member of the series C_nH_{2n+2}. In further attempts to eliminate the hydrocarbon with less hydrogen, the remainder of the oil after analysis was treated several times with hot nitric and sulphuric acids, and boiled repeatedly with sodium until there was no residue left on distillation. Although the boiling point was not materially changed by this treatment, analysis showed a decrease in the percentage of carbon to 83.91 per cent, and an increase in hydrogen to 16.10 per cent.

As in the Ohio oil, we found that distillates collected with much persistence between 120°–126°; after the eleventh distillation, the following weights were obtained: —

	120°-121°	121°-122°	122°-123°	123°-124°	124°-125°	125°-126°	126°-127°	127°-128°
Grams	85	70	80	60	30	30	70	60

The quantities between 122°–125° were not greatly diminished after the sixteenth distillation; and, like the distillates from the Ohio oil, these products contained small quantities of the aromatic compounds; they will receive further attention with reference to their chemical reactions. After the twelfth distillation, 110 grams of an oil collected at 126°–128°, bar. 752 mm., which was carefully purified in the manner already described. It gave, by the method of Victor Meyer, a vapor density corresponding to octane, C_8H_{18}; found, 4.24; required, 3.95. What has been said concerning the presence of the octanes in Ohio petroleum applies also to these distillates from Canadian oil, and they evidently require further study. The fractions collected at 130°–142° will be considered with the aromatic series. A distillate persisted at 145°–146°, as shown by the quantities collected at the twentieth distillation: —

	142°-143°	143°-144°	144°-145°	145°-146°	146°-147°	147°-148°
Grams	30	32	50	75	25	22

Since the fractions 144°–146° resisted all attempts to separate them into bodies with higher and lower boiling points, further study is necessary to determine whether they represent an individual product.

Between 149°–152°, 160 grams collected at the tenth distillation, a large portion of which distilled constant at 150°–151°, bar. 749 mm. After treatment with nitric acid and sodium, with results similar to those observed in the Ohio oil, this product gave, in a vapor density

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determination, a value required for nonane; found, 4.56; required for C_9H_{20}, 4.43. Distillation of the fractions from Canadian petroleum above 160° cannot be continued under atmospheric pressure without decomposition, probably caused by the action of air upon the hot oil. Unless, indeed, as some attempts have shown, it will be possible to distil them in an atmosphere of carbonic dioxide. These fractions have been distilled several times *in vacuo*, and further study of them is reserved.

From the results thus far obtained, it seems that the series C_nH_{2n+2} is represented in Canadian oil by the same members as are found in Ohio and Pennsylvania oils, but the lower hydrocarbons are present in much smaller proportions. The peculiar properties of Canadian oil depend, at least partially, on the small quantities it contains of the hydrocarbons C_nH_{2n+2}. The sulphur compounds exert an important influence. The presence of unsaturated hydrocarbons is not yet determined. Whether other series of bodies characterized by their instability form important constituents of the oil can only be ascertained by a critical study of the portions with high boiling points.

Aromatic Hydrocarbons.

Series C_nH_{2n-6}.

Benzol.

In looking for members of the aromatic series, the same methods were followed as in fractions of the Ohio oil. At the end of the eighth distillation, 20 grams collected at 77°–79°, 15 grams at 79°–81°, and 30 grams at 81°–83°. In treating these fractions, which contain benzol, with nitric acid under the conditions necessary for the formation of nitrobenzol, avoiding loss, so far as possible, and distilling off the unaffected hydrocarbons, the first fraction gave 2.8 per cent of benzol, the second 4.4 per cent, and the third 4.14 per cent. The benzol calculated from these data, in the total weight of the fractions, gave three grams as the total weight in the 64.5 kilos of crude oil taken, equivalent to 0.0047 per cent. Practically all the benzol was collected within these limits, since scarcely any nitro product was obtained in the higher and lower fractions. The quantity of benzol in the crude oil is probably somewhat larger than is here represented, although it must be considered as somewhat less than the amount contained in Ohio oil. Some loss undoubtedly resulted from distillation *in vacuo*, as well as in the subsequent separations. The

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nitrobenzol was recognized by conversion into aniline, which gave its characteristic reaction with furfurol.

Toluol.

In the portions containing toluol, between 107°–109° after the eighth distillation, the distillates amounted to 40 grams, at 109°–111° to 250 grams, and at 111°–113° to 50 grams. These fractions were treated for the formation of nitrotoluol in the same manner as those previously examined, and the fraction 109°–111° gave a weight of unaffected hydrocarbon and nitro product equivalent to five per cent of toluol in the fraction 107°–109° one per cent, and in the fraction 111°–113° one per cent. The higher and lower fractions gave no nitrotoluol. Referred to the total weights of the fractions, the quantity of toluol was 3.4 grams, equivalent to 0.005 per cent of the total weight of crude oil taken. As in the case of benzol, it is probable that the quantity of toluol is somewhat larger than is shown by these determinations. This product was shown to be toluol by conversion of the nitro derivative into toluidine, which gave characteristic color reactions.

Xylols.

The single allusion to the presence of xylols in Canadian petroleum is a general statement by Schorlemmer that he obtained reactions for benzol and its homologues, although the only aromatic hydrocarbon he separated was cumol in the form of the trinitro derivative.

After prolonged distillation, having found that fractions collected within limits corresponding to the boiling points of the xylols, we have spent considerable time in the formation of characteristic compounds as adequate evidence of their presence in the crude oil. In the twentieth distillation, within one degree after the twelfth, the following weights collected between 136° and 143° : —

	136°–137°	137°–138°	138°–139°	139°–140°	140°–141°	141°–142°	142°–143°
Grams	30	40	25	40	25	47	30

On account of the close proximity of the xylols in boiling points, it would evidently require much longer time in distillation and larger quantities of the distillates to separate them completely. We therefore depended upon the formation of derivatives that are sufficiently well characterized to warrant conclusions concerning the xylols from which they were formed. As a qualitative test for paraxylol, a part of the fraction 137°–138° was heated with nitric and sulphuric acids,

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and the oil which separated was allowed to stand until a crystalline product formed. After crystallization from alcohol, the nitro derivative thus obtained melted at 139°–140°, the melting point of trinitro-paraxylol. Another portion of the same fraction was boiled during several hours with chromic acid, and the solution extracted with ether. Upon evaporation, a white powder remained that sublimed without melting, and resembled in its appearance terephthalic acid. To determine the quantity of paraxylol according to the method suggested by Levinstein, a measured portion of the fraction 137°–138° was shaken during thirty minutes with concentrated sulphuric acid. The loss in volume corresponded to 10.77 per cent, representing the other aromatic hydrocarbons. The residual oil was then agitated with fuming sulphuric acid to dissolve the paraxylol, with a diminution in volume representing 9.02 per cent of the xylol.

The quantity of metaxylol in fraction 139°–140° was found by treating it first with dilute nitric acid, which, according to Brückner,* should not affect metaxylol, and distilling with steam, which carries over the metaxylol. The loss in volume, 7.5 per cent, was noted, and the distillate was agitated first with ammonia, then with concentrated sulphuric acid; the last diminution represented 8.8 per cent of metaxylol.

Many attempts were made to prove the presence of orthoxylol by the formation of the nitro compounds, and toluic acid. But no di- or tri-nitro compounds could be separated after treatment with nitric acid except those whose melting points corresponded to metaxylol. By the action of dilute nitric acid, which should not affect metaxylol, an acid was formed, but not in sufficient quantity to show that it was toluic acid. In forming the sulphonic acids and the sodium salts, so far as could be observed, no sodium orthoxylolsulphonate was present. It is quite possible that orthoxylol could be detected in a larger quantity of product. The larger amounts of the fractions 140°–142° therefore consisted partially of metaxylol. Referring the quantities of meta- and para-xylol to the weights of crude oil, the amount of paraxylol is 0.006 per cent, of metaxylol 0.003 per cent, in their respective fractions. These numbers cannot be assumed to represent more than an approximate estimation of these xylols, although they are doubtless, for the most part, collected in the fractions 137°–143°. In fractions 141°–143° the amount of sodic xylolsulphonate formed corresponded to 0.009 per cent of xylol, and, since orthoxylol could

* Ber. der deutsch. chem. Gesellsch., 1876, p. 405.

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not be detected, this quantity should be added to the total amount of metaxylol in the crude oil. Even then 0.012 per cent is scarcely more than a trace of this body. As in the similar determinations in Ohio oil, these results serve to show the very small proportion of the xylols contained in the crude oils. In the distillates 130°–140° of the Canadian oil there were indications of bodies capable of forming nitro products, but much larger quantities of these fractions will be needed for their separation.

Series C_nH_{2n}.

The fraction 68°-69° of the twelfth distillation was carefully purified with alcoholic mercuric chloride, nitric acid, sulphuric acid, and distillation with sodium. A combustion then gave the following results: —

0.1889 gram of the oil gave 0.5784 gram CO_2 and 0.2719 gram H_2O.

	Required for C_6H_{14}	Required for C_7H_{14}	Found.
C	83.71	85.71	83.45
H	16.28	14.28	15.99

This fraction therefore consisted essentially of hexane, and it contained no appreciable quantity of hexahydrobenzol.

The fraction 97°–98°, by the action of a mixture of nitric and sulphuric acids, gave a nitro compound heavier than water, equivalent to 10 per cent of the weight taken. The heavy oil turned red with sodic hydrate, and partially dissolved, reprecipitating with acids. By reduction with tin and hydrochloric acid, a substance with the properties of an amido compound was formed. It distilled with steam, was soluble in acids, and was precipitated from the acid solution by sodic hydrate. The prolonged fractional separation excluded benzol, and furthermore the amido derivative gave no reaction with furfurol. In its behavior toward sodic hydrate the nitro compound resembled the unsaturated nitro compounds of the series C_nH_{2n}, but the quantity of the distillate was not sufficient for complete verification. Another portion of the same fraction was heated during several hours with dilute nitric acid, the solution neutralized with sodic hydrate, and evaporated to dryness. A portion dissolved in water gave, with ferric chloride, the characteristic color for acetic acid, and more of the sodium salt, decomposed with hydrochloric acid and extracted with ether, gave colorless prismatic crystals resembling succinic acid.

In a distillate 95°–100°, from the Caucasus petroleum, Beilstein and

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Kurbatoff * observed the formation of acetic acid, considerable succinic acid, and other non-volatile acids. The oil remaining after the treatment with nitric acid, was distilled with sodium, and a combustion gave the following results already stated on page 56 : —

	Required for C_7H_{16}.	Required for C_7H_{14}.	Found.
C	84.00	85.71	84.31
H	16.00	14.28	15.77

Since hexahydrotoluol is not affected by nitric acid, but is completely decomposed by a mixture of nitric and sulphuric acids, it cannot be present in any appreciable quantity in this fraction.

In examining the fraction 118°–119° for hexahydroisoxylol, after the sixteenth distillation it was heated with a mixture of nitric and sulphuric acids. The acid was much colored from decomposition, and crystals separated which were very sparingly soluble in alcohol. The purified substance melted at 178°, the melting point of trinitroisoxylol. Hexahydroisoxylol was therefore present, although it formed but a small part of this distillate, as shown by the results of combustions repeated from page 56. It should be borne in mind that the oil analyzed was purified with nitric and sulphuric acids separately : —

	Required for C_8H_{18}.	Required for C_8H_{16}.	Found. I.	Found. II.	Found. III.
C	84.20	85.71	84.35	84.61	84.33
H	15.79	14.28	15.12	15.28	15.01

By further treatment with the acid mixture the hexahydro compound was sufficiently removed to prove the presence of a hydrocarbon C_nH_{2n+2}, as shown by the results of analysis already given.

With the limited quantity of distillates 136°–138°, which should contain hexahydromesitylene if it is a constituent of Canadian petroleum, remaining from the examination of the xylols, satisfactory conclusions could not be reached concerning the presence of this hydrocarbon. Since Markownikoff has recognized it in the Russian oil, it is very possibly present in the Canada oil. As in the Ohio fractions, after removing the xylols by continued action of the acid mixture, we obtained a small quantity of an oily nitro product that did not crystallize. With a larger supply of this distillate, further attempts will be made.

The lines of study which are now in progress on the Ohio and

* Ber. der deutsch. chem. Gesellsch., 1880, p. 1820.

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Canadian oils have been indicated in the preceding pages. Besides the higher vacuum distillates sodium salts of acids have been separated whose composition is now being determined. The facts thus far accumulated are not sufficient to determine whether the acids exist as such in the oils, as is maintained by Aschan, or whether they are oxidation products of other constituents, as Engler and Lachowitz believe. Since sodium salts have been obtained which contain much nitrogen and give the characteristic odor of pyridine compounds when heated, the possibility of pyridine carboxylic acids is suggested. In searching for the oxygen and nitrogen compounds we have separated bodies that give with nitric acid a brilliant red color, similar to what was early observed in our study of the sulphur derivatives.

The characteristic qualities of Canadian petroleum which appear in the results of this examination may be summarized as follows: —

1. In its high specific gravity and in the proportions that distil at different temperatures, Canadian petroleum approaches the Russian oil more nearly than the Ohio petroleum. But the specific gravity of the distillates is lower, approaching those of Ohio oil. As indicated by its lower specific gravity, Oil Springs oil is essentially different from Petrolia oil. This is especially evident in the lower percentage of sulphur, the larger quantities of the distillates, the higher specific gravity of these distillates, and the higher bromine absorption.

2. Petrolia oil is composed principally below 150° of members of the series C_nH_{2n+2}, although in much smaller quantities even than in Ohio oil. Another series is present capable of forming nitro products resembling the nitro compounds of the series C_nH_{2n+2}, or the unsaturated hydrocarbons C_nH_{2n}.

3. The aromatic hydrocarbons C_nH_{2n-6}, benzol, toluol, para- and meta-xylol are present in minute proportions. The hexahydro series is represented by hexahydroisoxylol, and probably by higher members.

4. By the behavior of the distillates toward bromine, the presence of hydrocarbons capable of forming addition products is indicated, as well as the formation of unsaturated hydrocarbons due to cracking in the distillates above 200° or 250°.

5. As in Ohio oil, the sulphur compounds have a tendency to collect in the higher fractions.

In the prosecution of this work I have received valuable aid from my assistants, Messrs. Cleveland, Little, and Giessen, and in portions of the work on the Canadian petroleum, from Mr. W. H. King, a student in this Laboratory.

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Origin of Petroleum.

In the clear and concise statement of the present condition of the theoretical discussion concerning the formation of petroleum by Professor Edward Orton (Geological Survey of Ohio, 1890), without including the thory of Mendelejeff that highly heated iron or iron carbides within the earth may furnish the world's supply, it is explained that most geologists accept the view that organic matter of vegetable or animal origin constitutes the source, and that it was deposited during the formation of the rock strata. Many insist on substances of vegetable origin as the chief source, and depend upon destructive distillation as an essential agency. A small minority of the geologists, and some chemists, especially the Germans, hold that animal remains may be accepted as the sole source in a process of primary decomposition without distillation.

The chief difficulty in arriving at any satisfactory conclusion concerning the formation of petroleum depends upon the fact that the principal process is completed, and there remains scarcely a trace of the stages through which the original substances have passed; or indeed these stages may have been so simple that we have before us in the oil rock all the indications that could ever have been observed concerning the formation of petroleum. Prevailing opinions seem to refer the genesis of the limestone oils to the decomposition of animal remains, and that of other oils to vegetable decomposition.

The most interesting observation on the natural formation of oil that has come to my knowledge is the experience of Mr. R. A. Townsend, of Petrolia, who has recently returned from India, where during fourteen years he has been engaged by the British government in prospecting for minerals and oils. In the oil region of Assam, Beloochistan, and the Punjaub, the surface is bare rock, and the anticlinals are easily located. Approaching an elevation while prospecting, he found at the top a bell-shaped depression, into which he descended to a vertical depth of 2,000 feet, and came upon beds of Tertiary oysters from which petroleum was exuding. The excavation had been formed by a thermal spring that had disappeared, leaving the strata bare. No oil was observed above or below the oyster beds. In oil territory owned by Mr. Townsend in Assam, half decayed tree trunks greasy with oil have been excavated.

One of the serious difficulties for those who believe in destructive distillation is an adequate source of heat. Organic matter, animal or vegetable, decomposes readily enough when exposed to the air at ordinary temperatures, but the products are very different from petroleum.

In the early development of organic chemistry, the nature of the products resulting from the destructive distillation of various forms of organic matter was recognized. Dippel's oil distilled from bones contains the nitrogen compounds pyrrol, pyridine, and their derivatives. Reichenbach (Schweigger's Journal, LXI. 273) identified paraffine as one of the distillation products of animal and vegetable bodies.

As already mentioned, Warren and Storer established the presence of the hydrocarbons C_nH_{2n+2}, C_nH_{2n}, and C_nH_{2n-6} as distillation products of a lime soap prepared from menhaden oil. More recently Engler has also prepared the petroleum hydrocarbons by the distillation of menhaden oil under pressure. There can therefore be no question as to the ready formation of petroleum from animal bodies when decomposed with the agency of heat. But that the same

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products may be formed without the aid of high temperatures is not so easily demonstrated. That any considerable elevation in temperature has accompanied the formation of petroleum, at least in the limestones, is rendered extremely improbable by the condition of the oil rock. Sections of the Corniferous limestone from wells drilled at Petrolia exhibit very plainly the conditions of stratification, without the slightest indication of metamorphic action. The rock consists of alternate light and dark layers, the light portion being much more compact than the darker strata, which are more granular, and offer greater resistance to the drill. As our analyses show, the two varieties of rock do not differ essentially in their composition. The darker portions of the strata evidently contain more oil.

Concerning the question as to whether petroleums can be sharply divided as to their origin, the limestone oils having their source in the decomposition of organic matter of animal origin, and other petroleums in the decomposition of vegetable matter, more experimental evidence is necessary.

The absence of nitrogenous organic bodies in petroleum has been suggested, by the adherents of vegetable matter as the source, as a serious objection to its origin in the decomposition of animal bodies. It is true that in other oils than those found in the limestones the quantities of nitrogen hitherto found are extremely small, as already explained (page 16). As further evidence of the minute proportion of nitrogen in non-sulphur oils, we have determined this element in Chinese petroleum (1), in a colorless Italian petroleum (2), in Macksburg, Ohio, oil, 1,900 foot level (3), and in a peculiar light yellow Berea Grit oil, 500 foot level (4), from Archer's Fork, Ohio, that is at present refined in large quantities. The last named oil deposits paraffine when cooled to 10°.

Determinations by the Kjeldahl method gave the following results: —

	Trenton Limestone Oil.	Corniferous Limestone Oils.
(1) 0.10	(1) 0.26	(1) 0.16
(2) 0.014	(2) 0.23	(2) 0.18
(3) 0.035	(3) 0.21	(3) 0.21
(4) 0.023	(4) 0.13	
	(5) 0.35	
	(6) 0.08	
	(7) 0.07	
	(8) 0.05	
	(9) 0.05	
	(10) 0.16	
	(11) 0.05	
	(12) 0.06	

It is therefore evident that in general a higher percentage of nitrogen is a distinctive quality of the limestone petroleums.

As mentioned above, we now have in hand certain nitrogenous bodies extracted from Ohio petroleum which resemble derivatives of the pyridine bases. In our earlier work on the sulphur compounds in the limestone oils (These Proceedings, XXV. 228), there were indications that these petroleums contain certain ethereal oils of vegetable origin beside other oils resembling the terpenes. A question may therefore arise as to whether the limestone oils have been derived exclusively from organic matter of animal origin.

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Recently Zaloziecki (Ber. der deutsch. chem. Gesellsch., 1894, p. 2081) has separated from the sulphuric acid extract of Galician oil, bodies which he concludes indicate the presence in the crude oil of the terpenes or allied substances.

On chemical grounds it seems reasonable that changes in organic bodies during long periods of time with exclusion of air, under enormous pressure, are sufficient to explain the formation of petroleum. The modifications that have been observed in various forms of chemical reactions under high pressure would seem to indicate that organic bodies should be affected quite differently than under ordinary conditions. I have in view some experiments on the behavior of organic matter under continued high pressure, fifty to one hundred tons per square inch, for the purpose of ascertaining what changes, if any, may result.

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II.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

ON THE OCCLUSION OF BARIC CHLORIDE BY BARIC SULPHATE.

By Theodore William Richards and Harry George Parker.

Presented January 9, 1894.

It has been known for a long time that baric sulphate possesses the power of carrying down other substances with it during the process of precipitation. Many experimenters have investigated with more or less accuracy the conditions which determine the amount of the occlusion in different cases, and have sought to eliminate as much as possible the error which the occlusion must introduce into analytical results.* Long ago, Fresenius found that some of the imprisoned salts, which could not be set free by any amount of washing of the freshly prepared baric sulphate, might be partially dissolved by water or acid after the precipitate had been ignited. Recently J. J. Phinney † has shown that in some cases, perhaps in all, this purifying process is only partial; hence it becomes important to discover a new method which may yield more satisfactory results. As Fresenius pointed out long ago,‡ the dissolving of the sulphate in sulphuric acid does not answer when barium salts are occluded.

The occlusion of baric chloride, the salt which is most generally used as the precipitant of sulphuric acid, has long been recognized. In most text-books upon quantitative analysis one is directed to pour the baric chloride into the sulphuric acid, and not *vice versa ;* and it is generally understood that this precaution is in order to prevent as

* A partial bibliography of the subject is given by M. Ripper, Zeitschr. für Anorg. Chem., II. 36. See also Jannasch and Richards, Journ. f. prakt. Chemie, [Neue Folge,] XXXIX. 321, XL. 236; E. A. Schneider, Zeitschr. für Physikal. Chem., 1892, X. 425; Lunge, Journ. f. prakt. Chemie, XL. 239; F. W. Mar, Am. J. Sci., [3.], XLI. 288; P. E. Browning, Am. J. Sci., [3.], XLV. 399; J. J. Phinney, Am. J. Sci., [3.], XLV. 468; Richards, These Proceedings, XXVI. 258; XXIX. 67, etc.

† Am. J. Sci., [3.], XLV. 468.

‡ Zeitschr. Anal. Chem., IX. 52.

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much as possible the error in question. It is also generally known that when the precipitate cakes together upon ignition, the occlusion has been large, and the result will usually be too high. But no systematic series of determinations of the conditions of experiment, and no exact method for wholly eliminating the error, have been devised and executed; hence the present work was undertaken with the idea of solving these difficulties.

In the course of an extended series of experiments upon the atomic weight of copper * finished several years ago, the attempt was made to determine the sulphuric acid in cupric sulphate by means of the usual analytical method. In order to correct the result for the occlusion of baric chloride, the precipitate, after having been weighed, was fused in pure sodic carbonate; and the chlorine in the aqueous solution of the residual cake was determined, calculated as baric chloride, and subtracted from the total weight of the precipitate.

The result in question was still vitiated by two opposite errors, the solubility of baric sulphate, and an incorrect atomic weight of barium, and hence it was rejected at the time. Nevertheless, the method seemed to be of value, and the stated intention of investigating it more closely has at last been carried out.

The objects of the present work were as follows: —

First, to discover if an accurate determination of sulphuric acid may be made by substracting from the weight of the baric sulphate that of the baric chloride found in it; and

Second, to define the conditions which determine the amount of the occlusion, and thus to show how the error may best be avoided altogether.

A standard solution of pure sulphuric acid (containing 3.2 per cent of H_2SO_4) was used as the test substance, being weighed in tightly stoppered light glass bottles. The baric chloride used for its precipitation had been purified by repeated crystallization, and made up into another standard solution, which was used in appropriate quantities. The sodic carbonate was also recrystallized many times; and this substance, as well as the nitric acid and all other substances used in the chlorine determination, were proved to be free from the halogen.

The platinized brass weights used were standardized with great care, and the weighings were corrected to the vacuum standard. Due allowance was made in each case for the weight of the filter ash, and every precaution usual in ordinary analytical work was taken to in-

* These Proceedings, XXVI. 258.

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sure accuracy. It is convenient to state first the experiments which determined the true strength of the standard acid, although these were made at a later stage of the work, when more experience had been gained.

In order to secure a standard of comparison which should be wholly different from the method under investigation, the strength of the sulphuric acid was determined alkalimetrically. Weighed portions of the solutions were almost neutralized with weighed portions of very pure gently ignited sodic carbonate, which had been crystallized ten times successively in platinum vessels. This neutralization was conducted in dilute solutions, so that there might be no loss of substance from the active effervescence. The dilute solutions were then evaporated to small bulk in platinum dishes, and the small excess of sodic carbonate required to complete the neutralization was added in dilute standard solution, methyl-orange being used as the indicator. This method, which may easily be made to give results accurate to within the hundredth of one per cent (one part in ten thousand) was devised for use in the investigation upon copper.

(1.) 18.6132 grams of the sulphuric acid solution required 0.6254 gram of dry sodic carbonate and 12.30 cubic centimeters of sodic carbonate solution (1 c. c. = 0.001793 gram of the salt), or in all 0.6475 gram for its neutralization.

(2.) 20.3966 grams of the acid solution required 0.6761 gram of dry sodic carbonate and 18.50 cubic centimeters of solution — in all 0.7092 gram of salt — for its neutralization.

The results of these analyses are precisely identical, each showing the acid solution to contain 3.214 per cent of H_2SO_4. It was important now to determine whether under the most favorable circumstances similar results might be obtained from the usual method of precipitation. All the precautions necessary to make the occlusion of baric chloride as small as possible, which are discussed later, were practised, and a very slight excess only of baric chloride was used. The precipitates after long standing were washed with as little freshly distilled water as was necessary to free them from every trace of acid, and the filtrates (each measuring about a hundred and thirty cubic centimeters) were evaporated to very small bulk in platinum dishes, allowed to stand, and filtered through tiny filters in order to collect the baric sulphate which had been dissolved by the acid solution. Finally, the baric sulphate was all fused with pure sodic carbonate; and the aqueous extract was acidified with nitric acid. The chlorine was now precipitated as argentic chloride, which was collected and weighed upon a Gooch crucible.

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(3.) 10.2107 grams of the solution gave 0.7804 gram of impure baric sulphate, collected upon a washed filter and ignited after the method of Bunsen. In the filtrate was found 0.0011 gram of additional precipitate. Only 0.0007 gram of argentic chloride was obtained from the whole of this substance.

(4.) 10.2189 grams of the solution yielded 0.7821 gram of precipitate, collected and ignited in a Gooch crucible.* The filtrates yielded 0.0017 more, and the whole of the baric sulphate gave 0.0024 gram of argentic chloride.

If these two determinations are not corrected for the occluded baric chloride, they give results for the strength of the acid solution which respectively equal 3.215 and 3.221 per cent of H_2SO_4. When corrected for this error, they are reduced to 3.213 and 3.215; and the average of these corrected results, 3.214 per cent, is exactly equal to that found by alkalimetry.

It is evident that these experiments show clearly enough three facts: —

First, that, when the occlusion is small, the proposed method is capable of yielding results which are both consistent and accurate.

Second, that the solubility of baric sulphate may easily introduce an error of as much as one fifth of a per cent, even when this solubility is reduced to a minimum.

Third, that the strength of the standard solution being analyzed was very nearly 3.214 per cent.

These experiments do *not* show that the method is capable of giving a true result when the occlusion is large, nor do they show the circumstances which determine the amount of the intruding impurity. The first of these additional questions, which is suggested by the fact that pure baric chloride parts with some of its chlorine when heated in the air, will be treated next.

Throughout the following series of seventeen experiments the precipitation of the baric sulphate was conducted as usual very nearly at the boiling point of the solutions. The precipitates were digested for about an hour before filtering, and were each washed with nearly a litre of boiling water. The baric sulphate was always ignited with its filter paper; if the whole mass of the paper is charred by gentle heat before any active combustion is allowed, no trouble from reduction is

* When good asbestos is used, — and this is not always easy to obtain, — the Gooch crucible answers admirably for this purpose. Compare Jannasch and Richards, Mar, Browning, and Phinney, *loc. cit.* Ripper must have used a poor quality of asbestos (Zeitschr. Anorg. Chem., II. 36).

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encountered. In order to prove this, two portions of baric sulphate ignited with their respective filters were treated with a little sulphuric acid and ignited again. In neither case was a gain in weight observed. A comparison of experiment No. 3 with No. 4 shows the same fact; for in one of these experiments the precipitate was collected in the usual way, while in the other it was ignited in a capped Gooch crucible, where there was no chance of reduction.*

After the precipitate had been weighed, the chlorine present was determined in the manner used in Nos. 3 and 4. The results are given on the next page.

The reasons for the varied amounts of occlusion noticed in this table will be discussed later. At present it concerns us only to note that, while the variation in the uncorrected column is from 0.3198 gram (experiment No. 5) to 0.3247 gram (experiment No. 11), or 1.77 per cent, the corrected column shows an extreme difference of only 0.53 per cent (0.3192 in Nos. 5 and 12, to 0.3209 in No. 15). The seventeen experiments may be grouped into two series; one, where the occlusion is large, giving a corrected average of 0.3199 (Nos. 7, 8, 9, 10, 11, 12, 13); the other, where the occlusion is small, giving a corrected average of 0.3201 (Nos. 5, 6, 14, 15, 16, 17, 18, 19, 20, and 21). The close agreement of these averages is sufficient proof that the method is capable of giving satisfactory results even when the occlusion is very large, and hence that no essential amount of the occluded chlorine in baric sulphate is liberated upon ignition.

The individual variations are no doubt chiefly caused by the solubility of baric sulphate in the acid solution from which it came, as is the deficiency of nearly 0.5 per cent in the final average. It is to be noted that in Nos. 14, 15, 16, and 17, where the average is higher than the others, a large excess of baric chloride, which must diminish the solubility of the sulphate, was used. The amount dissolved was not determined in any case, as the results were intended to represent the usual method of analysis, and were rather to be compared with one another than with an absolute standard.

It is interesting to note, however, that when the precipitation is conducted with reasonable care — as in Nos. 14 to 21, — the

* This observation does not agree with that of M. Ripper (Zeitschr. Anorg. Chem., II. 36). It is possible that Ripper conducted his combustion at too high a temperature; at any rate, it is true, as he observes, that a slight reduction would make much more difference in his work than in such as ours.

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TABLE OF RESULTS.

SERIES I.

No. of Experiment.	Amount of Solution taken.	Mixed Precipitate.	AgCl.	H_2SO_4 per 10 Grams of Solution.	
				Uncorrected.	Corrected.
5	12.1626	0.9262	.0025	.3198	.3193
6	11.6573	0.8913	.0032	.3211	.3203
7	13.4319	1.0306	.0091	.3223	.3202
8	11.8821	0.9096	.0071	.3215	.3197
9	10.1826	0.7866	.0143	.3244	.3202
10	10.1820	0.7844	.0137	.3236	.3194
11	10.1962	0.7881	.0152	.3247	.3201
12	10.2144	0.7870	.0149	.3236	.3192
13	10.2030	0.7887	.0133	.3246	.3207
14	10.1920	0.7800	.0039	.3214	.3202
15	10.2454	0.7853	.0032	.3219	.3209
16	10.2470	0.7840	.0039	.3214	.3202
17	10.2214	0.7828	.0046	.3216	.3203
18	10.1846	0.7789	.0039	.3212	.3200
19	10.1846	0.7788	.0042	.3212	.3199
20	10.2286	0.7850	.0057	.3223	.3206
21	10.2166	0.7812	.0052	.3212	.3196
True amount of H_2SO_4 present . .				.3214	

amount of the error due to occlusion usually almost balances the error due to the solution of the precipitate, so that the final uncorrected result closely approximates the true one. The average of these uncorrected results is 0.3215 instead of 0.3214.

Since the amount of argentic chloride obtained from four fifths of a gram of baric sulphate varied from 0.0005 gram (No. 3) to 0.0152 gram (No. 10), it becomes important to define the exact circumstances

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of the occlusion. Many of the experiments above were made with this idea in view.

The two experiments numbered 18 and 19 may be taken as types of the usual method of working. The volume of the sulphuric acid was about fifty, and that of the baric chloride about twenty cubic centimeters; the latter solution was slightly in excess, and was poured gradually into the former.

SERIES II.

No. of Experiment.	Mixed Precipitate.	Argentic Chloride.	AgCl per Gram of Precipitate.
	gram.	gram.	gram.
18	.7789	.0039	.0050
19	.7788	.0042	.0054
	Average		.0052

In order to determine whether an excess of baric chloride increases the occlusion, a similar series was made, using twice the amount of baric chloride necessary for the precipitation.

SERIES III.

No. of Experiment.	Mixed Precipitate.	Argentic Chloride.	AgCl per Gram of Precipitate.
	gram.	gram.	gram.
14	.7800	.0039	.0050
15	.7853	.0032	.0041
16	.7840	.0039	.0050
17	.7828	.0046	.0059
	Average		.0050

Since this average is not greater than the last (0.0052), no occlusion could have taken place after the precipitatation was complete, and the only effect of the excess of baric chloride was to diminish the solubility of the precipitate (see page 71).

In the next series the sulphuric acid was poured into the baric chloride, instead of *vice versa*.

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SERIES IV.

No. of Experiment.	Mixed Precipitate.	Argentic Chloride.	AgCl per Gram of Precipitate.
	gram.	gram.	gram.
9	.7866	.0143	.0182
10	.7844	.0137	.0175
11	.7881	.0152	.0193
22	.7832	.0156	.0199
	Average		.0187
	Average of Series II. and III. . .		.0051

These results prove the necessity of the old rule, which directs that the baric salt should always be added to the sulphate, if any proof of this was needed.

In all these experiments a small amount — perhaps the quarter of a cubic centimeter — of strong hydrochloric acid was added to the sulphuric acid before precipitation. In order to determine if this acid might have had some effect upon the occlusion, four experiments were made in which the amount of this acid was very much increased. In Nos. 12 and 13 about ten cubic centimeters of strong acid were used, and in Nos. 23 and 24 fully twenty. The first two were allowed to stand a

SERIES V.

No. of Experiment.	Mixed Precipitate.	Argentic Chloride.	AgCl per Gram of Precipitate.
	gram.	gram.	gram.
12	.7870	.0149	.0189
13	.7887	.0133	.0169
23	.7211	.0266	.0369
24	.7286	.0223	.0306
	Average		.0264
	Average of Series II. and III. . .		.0051

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long time, in order that the precipitate, which separates slowly from strongly acid solutions, might have time to deposit; while the second two were filtered within an hour, with the loss of nearly ten per cent of the precipitate.

Thus the presence of free hydrochloric acid increases the occlusion to an enormous extent.

In order to determine the effect of dilution, other circumstances remaining the same, two precipitations were made from solutions like those of Series II., diluted fourfold with water.

SERIES VI.

No. of Experiment.	Mixed Precipitate.	Argentic Chloride.	AgCl per Gram of Precipitate.
	gram.	gram.	gram.
25	.7676	.0023	.0030
26	.7701	.0024	.0031
	Average		.0031
	Average of Series II. and III. . .		.0051

Hence, the more dilute the solutions, the less is the occlusion.

In all the preceding cases the precipitate was allowed to run down the side of the beaker in an excessively fine stream, with continual stirring. This procedure had been shown in preliminary experiments to be even more efficacious as a means of diminishing occlusion than the addition of the precipitant in definite drops, no matter how slowly. Two experiments, in which the baric chloride was poured in with great rapidity, close the data to be presented.

SERIES VII.

No. of Experiment.	Mixed Precipitate.	Argentic Chloride.	AgCl per Gram of Precipitate.
	gram.	gram.	gram.
20	.7850	.0057	.0073
21	.7812	.0052	.0067
	Average		.0070

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As was to have been expected, the impurity is greater here than in Series II., III., and VI., but less than in Series IV. and V.

It was not the intention of this paper to extend the investigation to the study of the occlusion of other chlorides, which must necessarily complicate the problem greatly. It is very interesting to note that the amount of occlusion seems to be due rather to the amount of chlorine present than to the amount of barium, for hydrochloric acid increased the occlusion almost as much as an equivalent amount of baric chloride did. This observation leads one to conclude that a careful study of the phenomenon from a physico-chemical point of view might furnish some satisfactory clue as to the nature of such occlusion in general; and it is hoped that before long a collection of suitable data upon the problem may be obtained here.* The present paper deals only with the solving of an analytical problem.

At first sight, the facts shown by this paper appear to be contradictory to those stated by F. W. Mar,† who recommends the use of strong nitric and hydrochloric acids for the precipitation. It must be borne in mind, however, that Mar was precipitating the barium with an excess of sulphuric acid, and hence that a considerable amount of occlusion could make very little difference in his case. When one is determining sulphuric acid by means of an excess of barium, nothing could be worse than the addition of a large amount of hydrochloric acid; and this point cannot be too strongly emphasized.

Mar rightly states that a considerable excess of sulphuric acid is necessary to secure rapid precipitation of all the barium in strongly acid solutions. If Fresenius had realized that an excess of a common ion in solution decreases the solubility of a precipitate, he would not have confounded the solubility of baric sulphate in a strong solution of baric chloride with its solubility in pure water,‡ or in water containing free hydrochloric acid.

The conclusions reached in the present paper are as follows: —

First, that the occlusion of baric chloride by baric sulphate may lead to very serious error.

Second, that the amount of this occlusion is greater in concentrated than in dilute solutions, greater in the presence of hydrochloric acid than in its absence, and greater when the sulphate is poured into the

* For the treatment of an analogous case, see E. A. Schneider, Zeitschr. Phys. Chem., X. 425.

† Am. J. Sci., [3.], XLI. 288, XLV. 399.

‡ Zeitschr. f. Anal. Chem., IX. 52.

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barium salt than when the pouring takes place in the opposite direction.

Third, that under the usual conditions of careful precipitation in the presence of a small amount of free acid, the error from occlusion is almost balanced by the solubility of baric sulphate in acids and water, which solubility must be considered in careful work.

Fourth, that the error due to this occlusion may be corrected with great exactness by determining the amount of chlorine held by the precipitate, and subtracting the corresponding amount of baric chloride from the total weight of the precipitate.

The occlusion of iron and other substances by baric sulphate is being further studied in this Laboratory.

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III.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

ON THE CUPRIAMMONIUM DOUBLE SALTS.

THIRD PAPER.

By Theodore William Richards and George Oenslager.

Presented June 9, 1894.

The work already done upon the double salts of cupriammonium* suggested the possibility of obtaining compounds of fluorine and iodine similar to those of chlorine and bromine.

Many attempts were made to prepare cupriammonium acetofluoride, $Cu(NH_3)_2FC_2H_3O_2$, with invariable failure. The methods and the proportions of the reagents were varied in every possible way; but nothing could be obtained beside cupriammonium acetate and ammonium fluoride. Cupriammonium fluoride itself is very difficult to prepare, because of its solubility; and it is not unnatural that the double salt should be more so. It will be remembered, moreover, that while cupriammonium acetobromide is very easy to obtain, the normal chloride is almost if not quite impossible by the wet way. We should expect the fluorine compound to be even less possible. Because of these continued failures, the work with fluorine was discontinued.

The investigation of the compounds of iodine proved much more fruitful, yielding the following new substances: —

(1.) $Cu(NH_3)_3IC_2H_3O_2$.

(2.) $7\ Cu(NH_3)_2(C_2H_3O_2)_2 . Cu(NH_3)_2IC_2H_3O_2$.

(3.) $3\ Cu(NH_3)_2 . I_2 4\ NH_3$.

(4.) $2\ Cu(C_2H_3O_2)_2NH_4C_2H_3O_2 . H_2O$, besides confirming the work of Foerster† on the following substances: —

(5) $Cu(NH_3)_2(C_2H_3O_2)_2$.

(6) $Cu(NH_3)_2(C_2H_3O_2)_2\ 2\frac{1}{2}H_2O$.

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* Richards and Shaw, These Proceedings, XXVIII. 247; Richards and Whitridge, These Proceedings, XXX. 458.

† Berichte der deutsch. chem. Gesellsch., XXV. 3416.

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(1.) Ammon-cupriammonium Aceto-iodide, $Cu(NH_3)_3IC_2H_3O_2$.

In preliminary experiments the following method was used for preparing this compound. Four grams of finely powdered cupric acetate were stirred with a mixture of ten cubic centimeters of water, twenty of alcohol, and eight of glacial acetic acid. Ammonia gas was then passed into the mixture until all the cupric acetate was dissolved and the color of the solution had become deep blue. After the addition of three and a half grams of ammonic iodide the solution was set aside to crystallize, and in about six hours large deep blue monoclinic plates, having a six-sided outline, separated out. These crystals were washed with alcohol, and then dried between filter papers as quickly as possible. The salt thus prepared is usually not very pure, hence subsequently more alcohol was used in the preparation, with better success. Even yet, however, there was much room for improvement.

After many systematic experiments, which need not be detailed, the following method was found to yield very excellent results. Twelve grams of cupric acetate were dissolved in fifty cubic centimeters of ammonia water (sp. gr. = 0.90) in a flask. After cooling, thirty cubic centimeters of aqueous acetic acid (57 per cent) were added to the solution, then six grams of ammonic iodide, and finally fifty cubic centimeters of alcohol. Upon boiling over the water bath the mixture yielded a clear deep blue solution, which deposited crystals of ammon-cupriammonium aceto-iodide upon slow evaporation in the air. The first very small crop of crystals deposited upon cooling was not analyzed. The second served for Analysis IV. below, and the third crop, which was altogether the purest and best defined in crystalline form, served for Analyses V. and VIII. The substance used in Analyses I., II., III., VI., and VII. was prepared by earlier less satisfactory methods; it was undoubtedly the same substance, however.

Ammon-cupriammonium aceto-iodide consists of brilliant deep blue monoclinic crystals. It is not very permanent in the air, although much more so than its chlorine and bromine analogues. Upon exposure for a long time the crystals become dull and dark in color, and the substance slowly loses in weight. Water at once decomposes it, some of the copper going into solution, and the rest remaining as a basic precipitate. Acids set free iodine and precipitate cuprous iodide, as might be expected. The only unexpected property of the salt is the fact that it contains no crystal water, thus not maintaining a strict analogy with the corresponding chlorine and bromine compounds

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$Cu(NH_3)_3ClC_2H_3O_2 . H_2O$ and $Cu(NH_3)_3BrC_2H_3O_2 . H_2O$. The reason for this anomaly remains obscure.

The ammonia present in the compound was determined by distillation with pure potash or soda, the distillate being titrated with standard acid. It is convenient to prepare the alkali for this purpose directly from metallic sodium or from sodium amalgam, thus avoiding the complications in the subsequent proceedings introduced by the usual impurity of chlorine in commercial potash and soda. The residue in the distilling flask after the ammonia had been expelled was filtered, and to the filtrate was added a little sulphurous acid to reduce any iodate which might have been formed. Argentic nitrate was then added, and subsequently the argentic oxide and sulphite were dissolved by nitric acid, the argentic iodide being collected and weighed upon a Gooch crucible. In Analysis IV. the alkali was nearly neutralized, and in Analysis V. the solution was just acidified by pure nitric acid before the precipitation. In every case enough nitric acid was added after the precipitation to insure the solution of all but argentic iodide. and the agreement of the results is sufficiently satisfactory. The copper was determined by the electrolysis of the cupric sulphate obtained from the precipitated cupric oxide, which contained no trace of iodine; and the acetic acid was determined by combustion.

Analyses of $Cu(NH_3)_3IC_2H_3O_2$.

I. 0.2591 gram of the substance on distillation with potash required 25.34 cubic centimeters of decinormal acid for neutralization. gave on electrolysis 0.0545 gram of copper, and yielded 0.2042 gram of argentic iodide.

II. 0.2524 gram of the substance required 25.05 cubic centimeters of decinormal acid and gave 0.0527 gram of copper.

III. 0.2322 gram of the substance required 23.25 cubic centimeters of decinormal acid.

IV. 0.3960 gram of the substance gave 0.3109 gram of argentic iodide.

V. 0.2559 gram of the substance gave 0.2004 gram of argentic iodide.

(VI.) 0.3211 gram of the substance gave on combustion 0.0939 gram of carbon dioxide.

VII. 0.2946 gram of the substance gave on combustion 0.0864 gram of carbon dioxide.

VIII. 0.3062 gram of the substance gave on combustion 0.0907 gram of carbon dioxide.

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No.	Copper.	Ammonia.	Iodine.	Acetic Acid.
I. . . .	21.03	16.73	42.58	
II. . . .	20.88	16.95		
III. . . .	—	17.10		
IV. . . .	—	—	42.41	
V. . . .	—	—	42.31	
VI. . . .	—	—	—	19.62
VII. . . .	—	—	—	19.64
VIII. . . .	—	—	—	19.86
Averages .	20.96	16.99	42.43	19.71

	Calculated for $Cu(NH_3)_3IC_2H_3O_2$.	Found.
Copper	21.15	20.96
Ammonia	17.03	16.99
Iodine	42.19	42.43
Acetic acid	19.63	19.71
	100.00	100.09

(2.) Octocupriammonium Mono-iodide Acetate, $Cu_8(NH_3)_{16}I(C_2H_3O_2)_{15}$.

On allowing the mother liquor left over from the first method of preparing ammon-cupriammonium aceto-iodide to stand for a long time, large coal-black hexagonal crystals of unknown composition were deposited. Mixed with these were large blue crystals, which were separated mechanically from the black ones, and analyzed. The analysis corresponded closely with the formula

$$7\,Cu(NH_3)_2(C_2H_3O_2)_2 + Cu(NH_3)_2IC_2H_3O_2,$$

the complexity of which led to the suspicion that the crystals were a mixture instead of a definite compound. Nevertheless, upon qualitative testing, the smallest as well as the largest crystals were found to contain iodine.

In external appearance the crystals, which were usually at least half a centimeter in length, resembled those of cupriammonium acetate. An attempt was made to measure the angles of the crystals of each

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substance, but the faces were so covered with striations that the result was only partially satisfactory. For cupriammonium acetate the chief prism angle was about 70°, while for the complicated salt under consideration it was over 71° 30′. Even allowing a considerable margin for possible error, it would appear that the complicated salt must be a definite compound, and not merely cupriammonium acetate containing occluded cupric acetate and ammonic iodide. Another evidence of the probable definiteness of the salt is to be found in the fact that Richards and Moulton, in a paper yet to be published, have proof of the existence of a similar compound containing aniline and bromine instead of ammonia and iodine. The compound has no unexpected properties, and was analyzed in the usual fashion.

Analysis of $Cu_8(NH_3)_{16}I(C_2H_3O_2)_{15}$.

I. 0.2545 gram of the substance distilled with potash required 22.68 cubic centimeters of decinormal acid, gave 0.0333 gram of argentic iodide, and on electrolysis yielded 0.0707 gram of copper.

II. 0.2120 gram of the substance required 18.52 cubic centimeters of decinormal acid.

III. 0.2419 gram of another sample of the substance required 21.23 cubic centimeters of acid, and gave 0.0331 gram of argentic iodide and 0.0680 gram of copper.

No.	Copper.	Ammonia.	Iodine.
I.	27.78	15.25	7.07
II.	—	14.93	
III.	28.11	14.99	7.39
Averages . .	27.95	15.05	7.23

	Calculated for above Formula.	Found.
Copper	28.35	27.95
Ammonia	15.22	15.05
Iodine	7.07	7.23
Acetic acid (by dif.)	49.36	49.77
	100.00	100.00

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Every effort to make the normal cupriammonium aceto-iodide free from the acetate was unsuccessful; when so much of the ammonia has evaporated that $Cu(NH_3)_3IC_2H_3O_2$ ceases to form, the singular double salt which has just been described always makes its appearance.

(3.) Tetrammon-tricupriammonium Iodide,

$$3\,Cu(NH_3)_2I_2 + 4\,NH_3 = Cu_3I_6(NH_3)_{10}.$$

This interesting substance may be prepared by a method very closely resembling that used for preparing ammon-cupriammonium aceto-iodide. If eight grams instead of twelve of cupric acetate are used with fifty cubic centimeters each of ammonia and alcohol, thirty of acetic acid, and six grams of ammonic iodide, curious black crystals resembling irregular triangular pyramids make their appearance in the first place.

The new substance is similar in outward aspect to the corresponding bromine compound,* although less brilliant. The crystalline faces are so singularly marked and striated that an accurate crystallographic study would not be feasible. They possess a distinct bronze lustre which soon disappears owing to superficial decomposition. Upon exposure to the air the substance loses ammonia and iodine, finally leaving cuprous iodide. It is decomposed by water. Heated in aqueous or alcoholic ammonia it dissolves, forming a deep blue solution which upon cooling deposits bright blue needles remaining to be investigated.

From the mother liquors decanted from the black crystals may be obtained by further evaporation at first, $Cu(NH_3)_3IC_2H_3O_2$, and finally the mixture of $Cu_3(NH_3)_{16}I(C_2H_3O_2)_{15}$, with the coal-black hexagonal crystals already mentioned.† These latter crystals are very different in appearance from $Cu_3(NH_3)_{10}I_6$; they will be investigated in the future.

Analysis of $Cu_3(NH_3)_{10}I_6$.

I. 0.2049 gram of the substance yielded an amount of ammonia requiring 18.22 cubic centimeters of decinormal acid for neutralization, and 0.0352 gram of copper on electrolysis.

II. 0.2315 gram of the substance required 20.24 cubic centimeters of acid, and gave 0.0385 gram of copper and 0.2901 gram of argentic iodide.

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* Richards and Shaw, These Proceedings, XXVIII. 257.

† See page 81.

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III. 0.2302 gram of the substance required 20.36 cubic centimeters of acid, and gave 0.2872 gram of argentic iodide.

IV. 0.2307 gram of the substance required 20.35 cubic centimeters of acid.

V. 0.2150 gram of the substance on electrolysis gave 0.0367 gram of copper.

No.	Copper.	Ammonia.	Iodine.
I. . . .	17.17	15.19	
II.	16.63	14.94	67.73
III.	—	15.11	67.48
IV.	—	15.07	
V.	17.07		
Averages . .	16.96	15.08	67.61

	Calculated for above Formula.	Found.
Copper	17.00	16.96
Ammonia	15.20	15.08
Iodine	67.80	67.61
	100.00	99.65

(4.) Ammonic Dicupric Acetate, $NH_4Cu_2(C_2H_3O_2)_5 . H_2O$.

Since compounds containing three molecules of ammonia, one of acetic acid, and one atom of chlorine, bromine, or iodine had been proved to exist, it became a matter of interest to discover if it were possible to prepare $Cu(NH_3)_3(C_2H_3O_2)_2$, in which the halogen is replaced by acetic acid. Many unsuccessful attempts were made to obtain this compound. In the course of these experiments, however, a new double salt of cupric and ammonic acetates was discovered. Four grams of cupric acetate, six grams of glacial acetic acid, and twenty cubic centimeters of alcohol were mixed together, and ammonia gas was passed into the mixture until the green color just turns into blue. The solution became hot from the absorption of the ammonia, and the cupric acetate dissolved readily. After standing a few hours many small bluish green crystals were deposited, which have the com-

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position given below. The crystals are soluble in water without decomposition, and are fairly permanent in the air.

Analyses of $Cu_2NH_4(C_2H_3O_2)_5 . H_2O$.

I. 0.2586 gram of the substance yielded an amount of ammonia requiring 5.49 cubic centimeters of decinormal acid, and an electrolysis gave 0.0717 gram of copper.

II. 0.4303 gram of the substance required 9.40 cubic centimeters of decinormal acid.

III. 0.2525 gram of the substance gave 0.0703 gram of copper.

IV. 0.2604 gram of the substance required 5.52 cubic centimeters of acid, and gave .0725 gram of copper.

V. 0.3080 gram of the substance gave on combustion 0.2970 gram of carbon dioxide.

No.	Copper.	Ammonium.	Acetic Acid.
I.	27.73	3.84	
II.	—	3.96	
III.	27.86		
IV.	27.84	3.84	
V.	—	—	64.45
Averages . .	27.81	3.88	64.45

	Calculated for above Formula.	Found.
Copper	27.75	27.81
Ammonium	3.94	3.88
Acetic acid	64.38	64.45
Water (by difference)	3.93	3.86
	100.00	100.00

(5 and 6.) CUPRIAMMONIUM ACETATE.

This salt, discovered by Foerster,* may be prepared in an anhydrous condition by allowing an alcoholic solution of cupric acetate containing a slight excess of ammonia to evaporate in the air. Two determina-

* Ber. der deutsch. chem. Gesellsch., 1892, XXV. 3416.

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tions of the amount of copper present in the large deep blue crystals showed respectively 29.41 and 29.32 per cent, the theoretical being 29.48. The ammonia was found to be 15.68, instead of the theoretical amount 15.82 per cent, corresponding to the formula $Cu(NH_3)_2C_2H_3O_2$.

The crystallized salt containing two and a half molecules of crystal water, also discovered by Foerster, was prepared in blue feathery crystals by the evaporation of aqueous ammoniacal cupric acetate. Analysis showed the percentage of copper present to be 24.23 instead of 24.38, and the ammonia to be 13.02 instead of 13.08 per cent. The theoretical values were calculated for the formula

$$Cu(NH_3)_2(C_2H_3O_2)_2 \cdot 2\tfrac{1}{2}\, H_2O.$$

All of these compounds, as well as many similar ones obtained from other acids and the substituted ammonias, will be further studied at this Laboratory in the near future.

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IV.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

ON THE CUPRIANILINE ACETOBROMIDES.

By Theodore William Richards and Frederic Charles Moulton.

Presented June 9, 1894.

Recent investigations * have shown that double salts of cupriammonium containing two acids are easily obtainable in great numbers. It becomes a matter of interest to determine whether the substituted ammonias are capable of acting in the same way; and the present paper contains an account of the first experiments in this direction.

The only cupraniline compounds of which descriptions were found are three cuprosaniline compounds described by Saglier,† and cuprianiline chloride ($CuCl_2 2C_6H_7N$) described by Destrem.‡ Hence there was a wide field left open for the present investigation.

The compounds described in this paper are tabulated below.

(1.) $Cu(C_6H_7N)_2Br_2$.
(2.) $Cu(C_6H_7N)_2BrC_2H_3O_2$.
(3.) $Cu_3(C_6H_7N)_{16}Br_{15}(C_2H_3O_2)$.
(4.) $Cu_3(C_6H_7N)_{16}Br_{14}(C_2H_3O_2)_2$.
(5.) $Cu_3(C_6H_7N)_{16}Br_{13}(C_2H_3O_2)_3$.
(6.) $Cu_2(C_6H_7N)_4Br(C_2H_3O_2)_3$.
(7.) $Cu_3(C_6H_7N)_{16}Br(C_2H_3O)_{15}$.

Of these the simpler ones, Nos. 1 and 2, are undoubtedly definite compounds. Whether or not some of the others are isomorphous mixtures of these with cuprianiline acetate, which has not as yet been prepared in a pure state, it is hard to say.

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* Richards and Shaw, These Proceedings, XXVIII. 247; Richards and Whitridge, These Proceedings, XXX. 458; Richards and Oenslager, These Proceedings, XXXI. 78.

† Comptes Rendus, CVI. 1422.

‡ Bulletin de la Soc. Chim. de Paris, XXX. 482.

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(1.) Cuprianiline Bromide, $Cu(C_6H_7N)_2Br_2$.

This compound is formed as a brown powder whenever cupric bromide is added to an alcoholic solution of aniline; but a much more beautiful crystalline preparation is obtained when the solution contains acetic acid. For example, three grams of cupric bromide were dissolved in about forty cubic centimeters of alcohol; and to this were added twenty cubic centimeters of acetic acid and fifteen cubic centimeters of aniline. The mixture turned green immediately, and beautifully brilliant brown crystalline flakes of cuprianiline bromide were deposited. Nothing could be easier than the preparation of this substance.

From analogy to the cupriammonium compounds, one would have expected the cuprianiline aceto-bromide to have been formed under conditions given above; but this is not the case unless the solution contains a large per cent of cupric acetate.

Among a great number of samples of cuprianiline bromide, which have all given satisfactory analytical results, at least four colors have been observed. A few preparations consisted of long glossy black crystals, others consisted of dark brown shining flakes. Yet others were of a lighter brown, and some were almost of a golden yellow. Possibly the difference was due to variations in the thickness of the individual crystals.

The new compound is insoluble in alcohol and glacial acetic acid. When mixed with water it is decomposed at once into a basic bromide of copper, aniline hydrobromide, and a little free aniline. Alkalies and acids of course decompose it.

In order to prepare the substance for the electrolytic determination of the copper it was treated with nitric acid, evaporated to dryness, and ignited. The residue was dissolved in a mixture of nitric and sulphuric acids; the former acid was expelled on the steam bath, and the copper was separated in the usual fashion. Bromine was determined as argentic bromide; and the aniline was calculated from the amount of carbon dioxide yielded by the combustion of the compound. As a final check upon the results, the nitrogen present was determined according to the method of Dumas.

Analyses of $Cu(C_6H_7N)_2Br_2$.

I. 0.1978 gram of the substance yielded 0.0308 gram of copper.
II. 0.2299 gram of the substance yielded 0.0357 gram of copper.

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III. 0.2009 gram of the substance yielded 0.1842 gram of argentic bromide.

IV. 0.2530 gram of the substance yielded 0.2318 gram of argentic bromide.

V. 0.1028 gram of the substance gave 0.1313 gram of carbon dioxide upon combustion.

VI. 0.1705 gram of the substance yielded 10.20 cubic centimeters of moist nitrogen at 23° C. and 763.7 mm. pressure.

No.	Copper.	Bromine.	Aniline.	Nitrogen.
I. . .	15.57			
II. . .	15.52			
III. . .	—	39.02		
IV. . .	—	38.94		
V. . .	—	—	45.00	
VI. . .	—	—	—	6.77
Average	15.55	38.98	45.00	6.77

	Calculated for above Formula.	Found.
Copper	15.53	15.55
Bromine	39.04	38.98
Aniline	45.43	45.00
	100.00	99.53
Nitrogen	6.83	6.77

Many other similar determinations were made upon other samples, with similar results.

(2.) Cuprianiline Acetobromide, $Cu(C_6H_7N)_2(C_2H_3O_2)Br$.

This compound is formed with considerable difficulty, for the reaction tends to produce a compound containing either little or no acetic acid, or else little or no bromine. For the first time it was formed as follows. Three grams of cupric bromide were dissolved in about fifty cubic centimeters of alcohol, three grams of cupric acetate were dis-

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solved in ten cubic centimeters of commercial acetic acid, with the addition of twenty cubic centimeters of water; the two solutions thus formed were mixed, and fifteen cubic centimeters of aniline were added to the mixture. In about half an hour fine brown crystals began to separate out, and these crystals proved to be cuprianiline acetobromide. Subsequently a great deal of time was expended in attempting to repeat this experiment, with continued failure. At last a few of the original crystals were sprinkled upon the surface of a mixture like the one just described, at the time when the crystals were expected; and a large mass of the long sought for substance immediately separated. The reasons of the inconsistency of the first success and the subsequent failures remains to be discovered. It is possibly connected with variations in temperature.

The new compound is nearly insoluble in alcohol and glacial acetic acid, and is partially decomposed by water. Potassic hydroxide removes all the bromine from it only with difficulty. It is easily broken up by concentrated nitric acid, but not until heat has been applied.

Because of the stability of the compound it was necessary to determine the bromine in a rather elaborate manner. The sample was intimately mixed with a large amount of sodic carbonate in a porcelain crucible, covered with a thick layer of the same salt, pressed down very thoroughly, and very gradually brought to a red heat. As the mass contracted, more sodic carbonate was sprinkled around the edges of the mixture, to prevent the escape of a trace of bromine. The fused mass was dissolved in hot water, and the sodic bromide was filtered off and determined as usual.*

Analyses of $Cu(C_6H_7N)_2C_2H_3O_2Br$.

I. 0.2100 gram of the first sample of substance yielded 0.0343 gram of copper upon electrolysis.

II. 0.1768 gram of the first sample of substance yielded 0.0860 gram of argentic bromide.

III. 0.1743 gram of the second sample of substance yielded 0.0866 gram of argentic bromide.

IV. 0.1232 gram of the second sample of substance yielded 0.0600 gram of argentic bromide.

* This method was found to give the same results as that of Carius with these compounds. Of course the method would not answer if the bromine were directly combined with carbon.

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	Calculated for above Formula.	Found. I.	II.	III.	IV.
Copper	16.38	16.33			
Bromine	20.70		20.70	21.14	20.80

(3.) Octocuprianiline Monoacetobromide, $Cu_8(C_6H_7N)_{16}Br_{15}(C_2H_3O_2)$.

This substance has been made repeatedly as follows. Two grams of cupric bromide were dissolved in a hundred cubic centimeters of alcohol, and one and eight tenths grams of cupric acetate were dissolved in ten cubic centimeters of acetic acid, with the addition of just enough water to effect the solution. The two solutions were mixed, and fifteen cubic centimeters of aniline were added. In a quarter of an hour the desired crystals separated out from the deep green solution. The crystals resemble fine gunpowder in appearance, and possess properties more nearly resembling those of compound No. 1 than those of compound No. 2.

Analyses of $Cu_8(C_6H_7N)_{16}Br_{15}(C_2H_3O_2)$.

I. 0.1158 gram of the substance yielded 0.0181 gram of copper.

II. 0.1158 gram of the substance yielded 0.0996 gram of argentic bromide.

III. 0.2000 gram of the substance yielded 0.1738 gram of argentic bromide.

IV. 0.2712 gram of the substance yielded 0.2354 gram of argentic bromide.

	Calculated for $Cu_8(C_6H_7N)_{16}Br_{15}C_2H_3O_2$.	Found. I.	II.	III.	IV.
Copper	15.62	15.71			
Bromine	36.82		36.58	37.06	36.94

(4.) Octocuprianiline Triacetobromide, $Cu_8(C_6H_7N)_{16}Br_{13}(C_2H_3O_2)_3$.

Once this compound was obtained by adding 1.86 grams of aniline to a mixture of 2.23 grams of cupric bromide and 2.0 grams of acetic acid in alcoholic solution. The second time it was obtained by adding a few crystals of this first preparation to a mixture similar to that used for preparing No. 2, just as it was on the point of crystallization. The properties of this substance resemble very closely those of the last; and its analysis was conducted in the usual manner.

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Analysis of $Cu_3(C_6H_7N)_{16}Br_{13}(C_2H_3O_2)_3$.

I. 0.1754 gram of the substance yielded 0.0278 gram of copper.

II. 0.1754 gram of the substance yielded 0.1318 gram of argentic bromide.

III. 0.2445 gram of the substance yielded 0.1865 gram of argentic bromide.

IV. 0.2200 gram of the substance yielded 0.1677 gram of argentic bromide.

	Calculated for $Cu_3(C_6H_7N)_{16}Br_3(C_2H_3O_2)_3$.	Found. I.	II.	III.	IV.
Copper	15.82	15.85			
Bromine	32.30		32.00	32.46	32.44

(5.) Dicuprianiline Acetomonobromide, $Cu_2(C_6H_7N)_4Br(C_2H_3O_2)_3$.

This substance is formed with comparative ease, and was often obtained in the unsuccessful attempts to prepare cuprianiline acetobromide (No. 2). Its preparation is more certain if somewhat less cupric bromide — two grams instead of three — is used in the mixture described under that head. This variation of desirable conditions was to have been expected. Dicuprianiline acetomonobromide may also be formed by adding acetic acid to an alcoholic solution of cupric bromide until the color of the solution has become green, and then adding the aniline as before. After several hours, in either case, the compound separates as a dark bluish-black powder, insoluble in alcohol and glacial acetic acid. It is not decomposed by water, and boiling concentrated potassic hydrate will only remove a very small part of the bromine. At a moderate heat it is surprisingly stable; but upon ignition it is decomposed with considerable violence. When brought in contact with a drop of hot concentrated nitric acid it is almost explosive in the energy of its decomposition.

Analysis of $Cu_2(C_6H_7N)_4(C_2H_3O_2)_3Br$.

I. 0.1849 gram of the substance yielded 0.0310 gram of copper upon electrolysis.

II. 0.2310 gram of the substance yielded 0.0560 gram of argentic bromide.

III. 0.2053 gram of the substance yielded 0.0515 gram of argentic bromide.

IV. 0.1168 gram of the substance yielded 0.2026 gram of carbon dioxide upon combustion.

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	Calculated for $Cu_2(C_6H_7N)_4Br(C_2H_3O_2)_3$.	Found. I.	II.	III.	IV.
Copper	16.82	16.77			
Bromine	10.57		10.32	10.69	
Carbon	47.61				47.31

(6.) Octocuprianiline Acetomonobromide, $Cu_8(C_6H_7N)_{16}Br(C_2H_3O_2)_{15}$.

This, the last compound on the list, is formed with great ease whenever a large excess of cupric acetate or acetic acid is added to cupric bromide in alcoholic solution and aniline is added to the mixture. It separates after about twenty-four hours as a fine bluish or brownish black powder, whose properties resemble very closely those of the previous compound.

Analysis of $Cu_8(C_6H_7N)_{16}Br(C_2H_3O_2)_{15}$.

I. 0.1540 gram of the substance yielded 0.0264 gram of copper upon electrolysis.

II. 0.5098 gram of the substance yielded 0.0338 gram of argentic bromide.

III. 0.3352 gram of the substance yielded 0.0212 gram of argentic bromide.

IV. 0.2117 gram of the substance yielded 0.0134 gram of argentic bromide.

V. 0.1983 gram of the substance yielded 0.3672 gram of carbon dioxide.

VI. 0.4346 gram of the substance yielded 28.8 cubic centimeters of moist nitrogen at 759.4 millimeters pressure and 23° C.

No.	Copper.	Bromine.	Carbon.	Nitrogen.
I. . . .	17.14			
II. . . .	—	2.82		
III. . . .	—	2.69		
IV. . . .	—	2.68		
V. . . .	—	—	50.51	
VI. . . .	—	—	—	7.46
Averages .	17.14	2.73	50.51	7.46

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COMPOUND No. 6.

	Calculated for $Cu_8(C_6H_5NH_2)_{16}Br(C_2H_3O_2)_{15}$.	Found.
Copper	17.18	17.14
Bromine	2.69	2.73
Carbon	51.04	50.51
Nitrogen	7.58	7.46

It is apparent that all the compounds described in this paper may be arranged in a series, based upon the formulæ so multiplied as to include eight molecules of the cuprianiline group $Cu(C_6H_7N)^{II}$. At one end of this list stands cuprianiline bromide, and at the other should stand cuprianiline acetate. Only six of the seventeen compounds necessary to fill out this scheme have been found: —

1. $Cu_8(C_6H_7N)_{16}Br_{16}$.
3. $Cu_8(C_6H_7N)_{16}(C_2H_3O_2)Br_{15}$.
4. $Cu_8(C_6H_7N)_{16}(C_2H_3O_2)_3Br_{13}$.
2. $Cu_8(C_6H_7N)_{16}(C_2H_3O_2)_8Br_8$.
5. $Cu_8(C_6H_7N)_{16}(C_2H_3O_2)_{12}Br_4$.
6. $Cu_8(C_6H_7N)_{16}(C_2H_3O_2)_{15}Br$.

These compounds exhibit a change in properties which corresponds to the progressive change in composition. The stability of the product and its difficulty of decomposition increases as the per cent of bromine decreases. The violence of the reaction with a drop of strong nitric acid increases in the same way. As the acetic acid increases and the bromine diminishes, the crystalline form becomes less and less evident, the first compound consisting of well marked crystals, and the last of an impalpable powder. The average color of the substance becomes blacker and bluer as one proceeds in the same direction. The preparation seems to depend upon two factors: in the first place, upon the relative proportions of cupric acetate and bromide taken at the start, and in the next place, upon the time required for the crystallization. When the conditions of temperature and dilution are such that crystallization takes place at once, a crystalline compound, rich in bromine, separates. When, on the other hand, many hours elapse before the substance appears, a powder very poor in bromine is formed. It is possible that the inversion temperature of these double salts may vary

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progressively, so that the use of a thermostat would be necessary to secure absolute certainty in the yield.

The possibility that most of these compounds might be mere mixtures has been already suggested; but it is evident that some at least must be definite compounds. The fact that in the case of Nos. 2 and 4 a few crystals of an earlier preparation were capable of starting the crystallization of the same substance in larger quantity, throws valuable light upon this point. The fact that most of the substances fit so closely into the series having eight atoms of copper as the basis seems to indicate a definite law; for the chances are decidedly against coincidence in this regard. The per cent of bromine is of course the best means of determining the agreement with the theory, and the agreement is very satisfactory. Each preparation appeared under the microscope to be perfectly homogeneous, so that if the substances are mixtures, the components must crystallize together.

From this series of compounds one would infer the possible existence of cuprianiline acetate, but many repeated trials to prepare this compound in a pure state ended in failure. Several different new compounds were obtained during this search, one of them probably having the formula $Cu_2(C_6H_7N)_3(C_2H_3O_2)_4$, for it contained 19.82 per cent of copper. Another compound, which consisted, like this last, of long light blue needles, contained only 19.10 per cent of copper; while two others, a brown and a black powder, contained respectively 21.80 per cent and 17.28 per cent. All of these compounds, together with others containing chlorine and iodine instead of bromine, and other substituted ammonias in place of aniline, will soon be investigated further at this Laboratory.

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V.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

THE CHEMICAL POTENTIAL OF THE METALS.*

By Wilder D. Bancroft.

Presented by C. L. Jackson, May 9, 1894.†

Nearly four years ago Overbeck and Edler‡ published the results of their experiments on cells consisting of two metals in a single salt solution. Liquid amalgams of zinc, cadmium, tin, lead, and bismuth were used as anodes, while mercury served always as kathode. The results were as follows: the electromotive force of these cells is a function of the metals forming the electrodes, and of the negative ion of the salt solution; it is independent of the nature of the positive ion so long as this is not the same as the anode. The values for the electromotive force coincide, within the limit of error, with those for the corresponding, constant, reversible cells of the Daniell type.

With the exception of the conclusion that the electromotive force is smaller when the cell is reversible in respect to the anode, these results have been confirmed by the experiments of Paschen§ and of Gore.‖ The observations permit of other deductions not drawn by the authors. If we consider cells of the type $M_1|RX|M_3$ and $M_2|RX|M_3$, where M_1, M_2, M_3 represent the electrodes, and RX a solution of the salt RX, the difference of the two electromotive forces gives the value of the cell $M_1|RX|M_3|RX|M_2$. By Poggendorff's law this is the same as the cell $M_1|RX|M_2$. From the figures of Overbeck and

* The first part of this paper has already been published, Zeitschr. f. ph. Ch., XII. 289, 1893.

† Before this paper could be printed there appeared the articles of Goodwin and of Neumann. I have rewritten the part covered by their work so as to take account of their results and the proper date of the paper in its present form is December, 1894.

‡ Wied. Ann., XLII. 209, 1891.

§ Ibid., XLIII. 568, 1891.

‖ Phil. Mag., [5.], XXXIII. 28, 1892.

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Edler we can calculate the values for the combinations of zinc, cadmium, tin, lead, and bismuth in different salt solutions. I have done this, and I give a few of the figures in Table I. The electromotive forces are expressed in volts, as will always be the case when nothing is said to the contrary. The first column gives the electrode, the metal to the left being the anode. The concentrations of the different solutions are not comparable, and are therefore omitted. I have raised the value given by Overbeck and Edler for Pb|Hg in NaI by 0.025 volts, and that for Bi|Hg in NaCl by 0.075 volt. There is no doubt in my mind that these two values had been affected by secondary causes, and that this correction was necessary in order to make them comparable with the other observations.

TABLE I.

Electrodes.	KCl.	NaCl.	KBr.	NaBr.	KI.	NaI.
ZnCd	0.374	0.365	0.369	0.352	0.374	0.367
ZnPb	0.564	0.558	0.548	0.534	0.559	0.557
ZnBi	0.797	0.789	0.782	0.767	0.781	0.789
CdPb	0.190	0.193	0.179	0.182	0.185	0.190
CdBi	0.423	0.424	0.413	0.415	0.407	0.422
PbBi	0.233	0.231	0.234	0.233	0.222	0.232

The result is surprising. The influence of the negative ion disappears, and, if we considered this table alone, we should conclude that the electromotive forces of the cells $M_1|RX|M_2$ depended on the nature of the electrodes only. The experiments from which this table was compiled showed that, when $M_2 = Hg$, the negative ion is of importance. It is clear that the metals separate into two classes, the distinction being in respect to the behavior towards the negative ion. From the figures of Overbeck and Edler it appears further that zinc and cadmium, for instance, give the same value in all solutions of halogens; but that this is not the case for solutions of sulphates and nitrates. The question arises whether this difference is due to errors of observation, or whether we have to do with a special property of the halogens. The question cannot be settled by a reference to any existing experiments. Gore * has made a series of observations recently; but

* Phil. Mag., [5.], XXXIII. 28, 1892.

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his measurements are so inaccurate that no conclusions can be drawn from them. The results of Paschen* with dropping mercury electrodes show signs of the same regularities which are found in Table I.; but the variations in the observations are so great that the matter cannot be said to be definitely settled. It seemed to me necessary to make measurements in order to clear up the following points. Does the effect of the negative ion disappear in certain cases? Is this a characteristic of the halogens only? What is the effect of the concentration? May one look upon these cells as the limiting cases of the constant, reversible cells of the Daniell type?

Most of the experimental work recorded in this paper was done in the chemical laboratory at Amsterdam, and I am much indebted to Prof. van 't Hoff for assistance in carrying out this research.

The metals used came from the collection of the laboratory. I did not purify them further owing to lack of time. For this reason the absolute value of some of the figures may not be correct; but that has no effect on the general laws, which alone interested me. I purified the mercury myself; but I did not succeed in keeping the surface bright very long. The salt solutions were made by weighing out carefully the amounts of salt necessary for the concentrated solutions, and the others were made from these by diluting to the required volumes. The measurements were made with the small Lippmann capillary electrometer. As normal element I used a Latimer Clark cell; its value was found by Herr Barendrecht to be 1.426 volts. I compared it from time to time with a Gouy cell, and found no change which amounted to more than a millivolt. As working cell I had also a Leclanché with about the same electromotive force as the Clark cell. Its variations were quite considerable, about 3%. The measurements against mercury were made in a small test tube which had a platinum wire melted into it; the others were made in a U tube or in an ordinary beaker. The metals, with the exception of platinum, were used in the form of rods or heavy wire. At first I polished them with sand-paper; but this proved disadvantageous, as the surface is brought into a state of stress by this which is incompatible with accurate measurements. I have found it profitable to cut away the surface with a sharp knife, and then to wipe the metal with a cloth. There is the danger of a piece of steel getting on the electrode; but in most cases this will not cling firmly, and will be removed by wiping. It is true that the surface tension of a metal is often changed temporarily

* Wied. Ann., XLIII. 568, 1891.

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by cutting off a piece; but experiment shows that this change passes away more quickly than that caused by rubbing. In order to obtain accurate figures the electrodes should not be jarred. In some experiments the electrodes can be moved about without any very noticeable effect; but in most cases the slightest tremor has a very great influence on the electromotive force. As a rule, the electromotive force of this type of cell increases on standing, more or less quickly, till it reaches a definite maximum, where it remains constant. It is this maximum which I have given in the tables, because it is always the same in different experiments, while the value first observed is very irregular. In two cases only have I done differently. With magnesium one can get almost any desired value, according to the way the measurement is made. Immediately after setting up, the value for Mg|Zn is about 0.56 volt. If the magnesium is left in the solution and the liquid stirred slightly, the value becomes 0.713 volt. If the liquid be stirred vigorously, the reading rises to 0.76 volt, and even higher. In the last two cases there is a violent evolution of hydrogen. I have taken the first value as the most probable, and consider it as possibly too high. In the literature the recorded figures for Mg|Zn lie between 0.53 and 0.80 volt. The reason for this discrepancy is, as I have just said, in the varying conditions. With lead it is a little different. One gets at first a definite value, which remains constant quite a while, and then increases slowly to a maximum which I have not determined. As this "stationary" value is an easy one to determine, I have measured it; it evidently corresponds to a well defined condition, and is therefore just as good for most purposes of comparison as the highest value. The probable error of the measurements is not over 0.01 volt in most cases, and has no effect on the general relations.

I now come to the experimental data. The concentrations are given in chemical units (gram molecules per litre). The single values are the averages of five to twenty observations. Table II. shows the effect of the concentration, Table III. the effect of the negative ion when the electrodes are any two of the metals Mg, Zn, Sn, Pb, or Bi. The measurements of Zn|Bi and Cd|Bi had one marked peculiarity. The electromotive force Cd|Bi was at first about 0.315 volt. This potential difference increased slowly but regularly till it reached the value given in the table. In all the cases which I have studied Zn|Bi and Cd|Bi are the only ones in which there were signs of any rational connection between the change of the electromotive force and the time. I wished to include aluminium in the list; but the purest Neuhausen

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TABLE II.

Electrodes.	Concentration.	KCl.	KBr.	K_2SO_4.
MgZn	$\frac{1}{10}$	0.562	0.561	0.562
MgZn	$\frac{1}{100}$	0.561	0.561	0.562
MgZn	$\frac{1}{1000}$	0 561	0.564	0.563
ZnCd	$\frac{1}{10}$	0.332	0.333	0.334
ZnCd	$\frac{1}{100}$	0.334	0.333	0.335
ZnCd	$\frac{1}{1000}$	0.334	0.332	0.333
ZnSn	$\frac{1}{10}$	0.655	0.654	0.655
ZnSn	$\frac{1}{100}$	0.656	0.654	0.655

TABLE III.

Electrodes.	KCl.	KBr.	KI.	K_2SO_4.	KNO_3.	KAc.	K_2CO_3.	K_2Oxal.
MgZn	0.562	0.561	0.563	0.562	0.562	0.563	0.565	0.562
MgCd	0.895	0.894	0.893	0.897	0.895	0.896	0.897	0.894
ZnCd	0.333	0.333	0.331	0.334	0.332	0.332	0 334	0.331
ZnSn	0.655	0.654	0.652	0.655	0.655	0.656	0.654	0.657
CdSn	0.326	0.327	0.323	0.323	0.325	0.325	0.323	
ZnPb	0.526	0.528	—	0.527	0.526			
CdPb	0.195	0.194	—	0.194	0.193			
ZnBi	0.829	0.829	—	0.832				
CdBi	0.496	0.497	—	0.497				

aluminium contains traces of iron and behaves almost like iron. In Table IV. I give the measurements for Zn, Cd, and Pt against mercury, and also the measurements for Cd|Pt in several solutions. The figures in this table are not very accurate, with the exception of those made against mercury in a halogen solution. While the measurements are very easy to make in KCl, KBr, or KI solutions, with the other salts there appear such large and apparently causeless variations that

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TABLE IV.

Electrodes.	KCl.	KBr.	KI.	K_2SO_4.	KNO_3.	KAc.	K_2CO_3.	$K_2Oxal.$
ZnHg	1.151	0.991	0.847	1.302	1.200	1.228	0.995	1.301
CdHg	0.818	0.659	0.515	0.969	0.867	0.898	0.664	0.967
Difference	0.333	0.332	0.332	0.333	0.333	0.330	0.331	0.334
HgPt	—	—	—	0.106	0.092	0.063	0.079	0.095
CdHg + HgPt	—	—	—	1.075	0.959	0.961	0.743	1.062
CdPt	—	—	—	1.076	0.963	0.959	0.741	1.067

I do not feel sure that there are not errors of 0.1 volt in spite of the fact that I have taken great pains to find the real values. The two points which are of importance may be considered as settled: the concentration has no effect, and the negative ion of the salt solution has

TABLE V.

Cd | KCl | Hg.

$\frac{1}{1000}$	$\frac{1}{100}$	$\frac{1}{10}$	$\frac{1}{1000}$	$\frac{1}{100}$	$\frac{1}{10}$
0.814	0.818	0.822	0.816	0.820	0.822
0.818	0.817	0.817	0.817	0.818	0.817
0.821	0.817	0.818	0.817	0.817	0.818
0.832	0.816	0.817	0.817	0.820	0.819
0.813	0.804	0.822	0.818	0.817	
0.822	0.821	0.817	0.818	0.817	
0.817	0.817	0.821		Averages.	
0.817	0.818	0.822	0.818	0.817	0.819

an influence both in the combinations Zn|Pt, Cd|Pt, and in Hg|Pt. In Table V. there is a complete series of observations on the effect of the concentration. I have made similar series with several other solutions; but as they gave the same result I do not communicate them. When in a halogen solution one of the electrodes is platinum, both the

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TABLE VI.

Concentr.	Hg | $BaCl_2$ | Pt.		Concentr.	Hg | $BaCl_2$ | Pt.	
	Found.	Calc.		Found.	Calc.
$\frac{1}{2000}$	0.158	0.158	$\frac{1}{100}$	0.193	0.194
$\frac{1}{1000}$	0.164	0.166	$\frac{1}{20}$	0.212	0.213
$\frac{1}{200}$	0.186	0.186	$\frac{1}{10}$	0.220	0.221

concentration and the nature of the solution have a great influence on the electromotive force. In Table VI. are the results for different solutions of barium chloride. The figures under the heading "Calc." are obtained from the formula

$$E_1 - E_2 = \tfrac{1}{2} RT \log \frac{C_1}{C_2},$$

allowance being made for the dissociation. The value for the $\frac{1}{200}$ normal solution is taken as the basis of the calculation; $R = 2$ and

TABLE VII.

Concentr.	Hg | KCl | Pt.		Hg | KBr | Pt.		Hg | KI | Pt.		Cd | KBr | Pt.		Hg | KCl | Pt.	
	Found.	Calc.	Found.	Calc.	Found.	Calc.	Found.	Calc.	Found.	Calc.
$\frac{1}{1000}$	0.152	0.152	0.233	0.233	0.388	0.387	0.893	0.892	0.127	0.127
$\frac{1}{500}$	0.164	0.164	0.245	0.245	0.400	0.399	0.905	0.904	0.138	0.139
$\frac{1}{100}$	0.190	0.190	0.271	0.271	0.425	0.425	0.930	0.930	0.165	0.165
$\frac{1}{50}$	0.201	0.201	0.282	0.282	0.436	0.436	0.943	0.941	0.179	0.176
$\frac{1}{10}$	0.227	0.227	0.308	0.308	0.463	0.462	0.967	0.967	0.201	0.202
$\frac{1}{5}$	0.238	0.237	0.319	0.319	0.473	0.473	0.977	0.978	0.212	0.213

$T = 290$. In Table VII. I give the figures for solutions of KCl, KBr, and KI. The change of the electromotive force with the concentration follows the formula

$$E_1 - E_2 = \tfrac{2}{3} R T \log \frac{C_1}{C_2},$$

using as before the value for $\frac{1}{100}$ normal as a starting point. I have given two series of determinations for Hg|KCl|Pt. In the first set of

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experiments I found only the smaller values. Repeating the measurements with other solutions I obtained chiefly the figures given in the first column, although now and then the values for the other series appeared. As I could not discover the reason for these sudden changes of 0.036 volt, I give both series, though I am inclined to regard the larger values as the more probable.

The first glance at the table reveals the striking regularity of the phenomena. Where the electrodes are any two of the metals Mg, Zn, Cd, Sn, Pb, or Bi, the negative ion has no effect; the electromotive force remains unaltered when the concentration changes from 10 to 1,000 litres. The influence of the negative ion is very marked in the cells where mercury forms one pole; but there is no sign of any effect due to the concentration. This appears first in the combinations with platinum, and then only in the solutions of the halogens. This abnormal behavior of platinum is, as Ostwald* has pointed out, probably due to a tendency to go over into chlor-, brom-, or iod-platinates, where the platinum is no longer present as ion. It is worth noticing that a similar result was not detected with mercury, though here there is a tendency to a partial formation of complex salts. Whether the greater accuracy of the measurements with mercury in solution of halogens is connected with the possible existence of complex salts, I do not know.

The relation between these single liquid polarizable cells and the corresponding, constant, reversible cells of the Daniell type must next be considered. According to the theory of Nernst, the potential difference between a metal and a solution of a salt of that metal is given by the expression

$$\pi = \frac{RT}{ne} \log \frac{P}{p} \times 10^{-4} \text{ volts},\dagger$$

where π is the potential difference, n the valency of the kation, p its partial osmotic pressure, e the quantity of electricity transported by a gram equivalent, and P the solution pressure of the electrode. The electromotive force of a cell of the Daniells type $M_1|p_1M_1X|p_2M_2X|M_2$ will be the algebraic sum of the two potential differences between the metals and the solutions plus the difference of potential between the liquids. I leave out of account a possible potential difference be-

* Lehrbuch der Allgem. Chem. (2 Aufl.), II. 897.

† Nernst, Zeitschr. f. ph. Chem., IV. 148, 1889.

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tween the metals, as this term is negligible so far as our present knowledge goes. The electromotive force of this type of cell will be

$$\pi = \frac{RT}{ne}\left(\log\frac{P_{M_1}}{P_{M_1}} + \log\frac{p_2}{p_1}\right) \times 10^{-4} + z,$$

where z represents the difference of potential between the solutions, and the valency of the metals M_1 and M_2 is the same. If the wandering velocities of the ions M_1 and M_2 are nearly equal, and p_1 and p_2 be made so, the value of z approaches zero, while the term $\log\frac{p_2}{p_1}$ drops out entirely. The electromotive force of the cell

$$M_1|pM_1X|pM_2X|M_2$$

is given very nearly by the expression

$$\pi = \frac{RT}{ne}\log\frac{P_{M_1}}{P_{M_1}} \times 10^{-4} \text{ volts},$$

and is independent of the absolute concentration of the salts M_1X and M_2X. Let us take as a concrete case the cell $Zn|ZnSO_4|CuSO_4|Cu$, and let the concentrations of the $ZnSO_4$ and $CuSO_4$ always be equal. It has been found experimentally that the electromotive force of this cell is independent of the absolute concentration.* Suppose that, instead of diluting the two solutions with pure water, we add a solution of potassium sulphate. According to Nernst's theory, this will have no influence on the eleetromotive force except in so far as it affects the dissociation of the two sulphates, and thereby the concentrations of the Zn and Cu ions. If the dilution be carried far enough, we shall come at last, without change of electromotive force, to the cell with neither zinc nor copper sulphate, to the cell

$$Zn|xZnSO_4 + xK_2SO_4|xCuSO_4 + xK_2SO_4|Cu,$$

which is the same as the cell $Zn|xK_2SO_4|Cu$. In other words, the one-liquid non-reversible cells are the limiting cases of the two-liquid reversible cells, in which the concentrations and wandering velocities of the reversible ions are equal, the dissociation being supposed to be complete. This last clause is necessary, for if the percentage dissociations of the zinc sulphate and copper sulphate were different,

* Wright, Phil. Mag., [5.], XIII. 265, 1882.

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equal concentrations of the two sulphates would not correspond to equal concentrations of zinc and copper ions, and this would affect the potential difference between the solutions. The concentration of the K_2SO_4 should have no effect, and it was shown in Tables II. and V. that this was the case. It is clear that in measurements made with two-liquid reversible cells, there are two sources of error besides those due to the surface conditions of the electrodes. These are differences of concentration and differences of wandering velocities. The effects of these two errors are that the terms $\log \frac{p_2}{p_1}$ and z do not disappear. The determinations made with single-liquid cells are free from these sources of error; but the difficulties due to polarization are so great that the variations are apt to be much larger than in measurements made with two-liquid reversible cells. In Table VIII. I give some of the results obtained with the two styles of cells. In the first four columns are the measurements of Paschen,* myself, Overbeck and Edler,† Ostwald,‡ all made with single-liquid cells. In the next three are the figures of Wright and Thompson,§ Neumann,‖ Braun,¶ with reversible cells. In the eighth are the data of Magnanini,** and in the ninth those of Regnauld,†† the former being for polarizable, the latter for non-polarizable cells. The agreement is not as striking as one might wish; but it is sufficient. The values marked with a star are not properly comparable, because the two solutions were not of the same concentration.

Nernst's formula for the cells we have been considering is

$$\pi = \frac{RT}{ne} \log \frac{P_{M_1}}{P_{M_2}} \times 10^{-4} \text{ volts.}$$

It is therefore necessary to discuss the nature of $\log P$. Nernst has not made any direct statement, so far as I know, about a possible connection between $\log P$ and the negative ion of the salt solution. Ostwald ‡‡ and his pupils look upon $\log P$ as a function of the electrode

* Wied. Ann., XLIII. 590, 1891.
† Ibid., XLII. 209, 1891.
‡ Zeitschr. f. ph. Chem., I. 583, 1887.
§ Phil. Mag., [5.], XIX. 1, 1885.
‖ Zeitschr. f. ph. Chem., XIV. 193, 1894.
¶ Wied. Ann., XVI. 575, 1882.
** Rend. Acc. Linc., VI. 182, 1890.
†† Wiedmann, Elektricität (2 Aufl.), I. 792.
‡‡ Lehrbuch, II. 855.

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TABLE VIII.

Electrodes.	Electrolyte.	Paschen.	W. D. B.	O. & E.	Ostwald	W. & T.	Neumann.	Braun.	Maganini.	D=100. Regnauld.
ZnCd	Chlorides	0.296	0.333	0.368	0.360	0.330	0.329	0.334	0.32	0.235
ZnCd	Bromides	0.293	0.333	0.364	0.340	0.315	—	0.256	0.30	0.235
ZnCd	Iodides	0.298	0.331	0.365	0.304	0.322	—	0.262	0.20	0.235
ZnCd	Sulphates	0.350	0.334	0.430	0.401	0.360	0.362	0.33–37	0.36	0.307
ZnCd	Nitrates	—	0.332	0.446	0.411	0.352	0.352	0.27–37	0.38	0.235
ZnCd	Acetates	—	0.332	—	0.373	—	—	0.336		
ZnPb	Chlorides	0.512	0.526	0.561	0.610	0.591*	0.598*	—	0.51	
ZnPb	Bromides	0.525	0.528	0.541	0.599	0.571	—	—	0.45	
ZnPb	Iodides	0.545	0.527(1)	0.558	0.587	0.455	—	—	0.38	
ZnPb	Sulphates	0.525	0.527	0.502	0.592	0.50–55*	—	—	0.51	
ZnPb	Nitrates	—	0.526	0.589	0.598	0.585	0.589	0.440	0.51	
ZnPb	Acetates	—	0.527(1)	—	0.638	0.607	0.601	0.54–58		
CdPb	Chlorides	0.216	0.195	0.192	0.249	0.260*	0.269*			
CdPb	Bromides	0.232	0.194	0.181	0.259	0.256				
CdPb	Iodides	0.247	0.194(1)	0.188	0.256	0.24*				
CdPb	Sulphates	0.18	0.194	0.17	0.191	0.13–17*				
CdPb	Nitrates	—	0.193	0.243	0.187	0.233	0.237	0.18–22		
CdPb	Acetates	—	0.194(1)	—	0.265	—	—	0.240		

metal and the temperature only, and hold that it is independent of the nature of the negative ion. If this be so, we ought to find that all cells of the type $M_1|pM_1|XpM_2X|M_2$ should have the same value so long as M_1 and M_2 remain the same, and that a change in X should have no effect, barring secondary disturbances such as differences of wandering velocity, of dissociation, etc. In the non-reversible cells $M_1|RX|M_2$, where these disturbing influences are eliminated, this should be even more noticeably true. That this is the case for certain metals I have shown in Tables II. and III. The results of other in-

(1) Values marked thus are calculated from the other experiments, and are not direct observation.

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vestigators, as given in Table VIII., show the same thing, though not quite so clearly. The values for Zn|Cu in solutions of chlorides, bromides, and iodides are found to be identical by Paschen, by Overbeck and Edler and by Regnault, though the three sets differ hopelessly in absolute value. Braun makes the bromides and iodides the same, and puts the chlorides, sulphates, and nitrates in a group together. There is not the same agreement among the reversible cells in which Pb forms one of the electrodes; but this is due in part to the insolubility of the lead salts. With the polarizable cells things are much clearer, though the discrepancies between the values found by different observers complicates matters very much. Ostwald finds practically the same value for Zn|Pb in all solutions except acetates. Paschen makes the bromides and sulphates the same, while Overbeck and Edler find the chlorides and iodides identical. On the whole, we may say that the theory of Nernst has predicted the facts with great accuracy so far. If, however, the single-liquid cells are the limiting cases of the two-liquid reversible cells, and if log P is a function of the electrodes and temperature only, the electromotive force should always be independent of the nature of the negative ion of the salt solution. That this is not so will be seen from Table IX.

TABLE IX.

Electrodes.	Electrolyte.	Paschen.	W. D. B.	O. & E.	Ostwald.	W. & T.
ZnHg	Chlorides	1.112	1.151	1.121	1.173	1.12–26
ZnHg	Bromides	0.983	0.991	0.996	1.036	0.972
ZnHg	Iodides	0.846	0.847	0.830	0.841	0.801
ZnHg	Sulphates	1.300	1.302	1.302	1.484	1.46–51
ZnHg	Nitrates	—	1.200	1.330	1.422	1.499
ZnHg	Acetates	—	1.228	—	1.451	
CdHg	Chlorides	0.816	0.818	0.755	0.813	0.812
CdHg	Bromides	0.690	0.659	0.632	0.696	
CdHg	Iodides	0.548	0.515	0.465	0.535	
CdHg	Sulphates	0.968	0.969	0.962	1.083	
CdHg	Nitrates	—	0.867	0.884	1.011	
CdHg	Acetates	—	0.898	—	1.078	

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The variation in passing from a chloride to an iodide solution is about 0.3 volt, far more than can be accounted for by any experimental error. This necessitates a reconsideration of the Nernst hypothesis to see where the flaw in the reasoning occurs. The assumption made is, that, if a metal be dipped into a solution of one of its salts, ions of that metal will go into solution, and the electrode become charged negatively towards the electrolyte if the "solution pressure" of the metal is greater than the osmotic pressure of the corresponding ion in the solution. If the osmotic pressure of the ion in the solution is greater than the "solution pressure," ions will be precipitated upon the metal, which will become positive to the solution. This same reasoning is applicable to zinc in a solution of potassium chloride, for instance. The initial concentration of the zinc ions in the solution is zero, and the metal will therefore send off ions until the potential difference corresponding to equilibrium is reached. This will not be the case when we consider mercury in a solution of potassium chloride. There are no mercury ions in solution to precipitate on the metal, and it remains an unanswered problem how the mercury is to become charged positively in respect to the solution. Yet this takes place, and the value as determined by the dropping mercury electrode method is a perfectly well defined one. This value should be independent of the nature of the salt solution if Ostwald's assumption about log P is correct. This is not the case. In this connection I wish to say that the question as to the value of the dropping mercury electrode as a means of measuring single potential differences does not affect this discussion at all. It is an experimental fact that the sum of the potential differences $M_1|RX$ and $RX|M_2$, as determined by this method, is equal to the electromotive force of the cell $M_1|RX|M_2$, and it is immaterial for the present purposes whether the single determinations are wrong by a constant amount, as I am only considering variations in the values. I will now try to show what conclusions may be drawn from the measurements of Paschen * on the potential differences between metals and salt solutions not containing the metal of the electrode as ion. He points out himself that the potential difference is not a function of the positive ion of the salt solution. It is not a function of the concentration. Paschen inclines to the opposite view; but I think he is wrong, and that his own results as tabulated in Table X. will bear me out. The first column gives the nature and concentration of the solution; the second, third, and fourth columns give the poten-

* Wied. Ann., XLIII. 590, 1891.

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tial differences between the metals mercury, zinc, and cadmium, and the solution. Mercury is positive towards the solution, zinc and cadmium negative.

TABLE X.

Solution.	Sol.|Hg	Zn|Sol.	Cd|Sol.	Solution.	Sol.|Hg.	Zn|Sol.	Cd|Sol.
HCl = 1 l.	0.560	0.560	0.248	HBr = 0.272 l.	0.503	0.393	0.175
= 10 l.	0.551	0.610	0.272	= 0.9833 l	0.490	0.423	0.202
= 100 l.	0.584	0.643	0.242	= 10 l.	0.493	0.567	0.238
KCl = 0.280 l.	0.524	0.525	0.260	= 100 l.	0.496	0.610	0.246
= 1 l.	0.539	0.547	0.249	KBr = 0.402 l.	0.474	0.399	0.203
= 10 l.	0.553	0.575	0.251	= 1 l.	0.483	0.441	0.186
= 100 l.	0.584	0.523	0.240	= 10 l.	0.493	0.422	0.167
NaCl = 0.239 l.	0.562	0.521	0.262	= 100 l.	0.505	0.496	0.183
= 1 l.	0.556	0.512	0.266	HI = 10 l.	0.411	0.427	0.117
= 10 l.	0.557	0.541	0.268	= 100 l.	0.417	0.515	0.159
= 100 l.	0.590	0.557	0.268	= 1000 l.	0.386	0.584	0.214
$MgCl_2$ = 0.971 l.	0.546	0.525	0.252	KI = 0.795 l.	0.400	0.250	0.113
= 2 l.	0.547	0.531	0.277	= 1 l.	0.400	0.233	0.113
= 20 l.	0.548	0.598	0.258	= 10 l.	0.412	0.308	0.110
= 200 l.	0.580	0.516	0.245	= 100 l.	0.412	0.389	0.120
$BaCl_2$ = 0.809 l.	0.562	0.512	0.259	= 1000 l.	0.386	0.454	0.199
= 2 l.	0.555	0.554	0.249	K_2SO_4 = 2.152 l.	0.700	0.618	0.287
= 20 l.	0.553	0.583	0.281	= 20 l.	0.720	0.573	0.274
= 200 l.	0.586	0.566	0.240	= 200 l.	0.730	0.592	0.252
H_2SO_4 = 2 l.	0.835	0.653	0.319				
= 20 l.	0.817	0.668	0.284				
= 200 l.	0.825	0.668	0.261				

The values for Sol|Hg are identical for dilutions of 11 and 101, with the exception of KCl, KBr, K_2So_4, and H_2SO_4; and the variations for K_2SO_4 and H_2SO_4 are in opposite directions, and certainly due to experimental error. There is also no reason to assume that KCl is

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theoretically different in behavior from NaCl or $BaCl_2$, and we must therefore conclude that this discrepancy is also accidental. In passing from dilutions of 101 to those of 1001, there is a distinct increase in potential difference between mercury and chloride solutions. With the other solutions the change is either non-existent or much less marked. On the other hand, cadmium shows this behavior only with HI and KI solutions, zinc with HCl, NaCl, HBr, KBr, HI, and KI solutions. The solutions of HBr, KBr, HI, and KI are not the ones where mercury shows a marked change of value with increasing dilution, so that there is no qualitative regularity in the phenomena. As there is also no quantitative connection to be detected between the change of concentration and the change of potential difference, and as the experimental error is very large in the case of determinations with dilute solutions, I see no reason to assume that there is any change of potential difference, at any rate within wide ranges of concentration.* I am led to this conclusion the more strongly because if we admit with Paschen that the potential difference increases with increasing dilution, we must admit that the electromotive force of the cell Cd|KCl|Hg is a function of the concentration, and I have already shown that this is not the case.

Paschen has pointed out that these potential differences are functions of the metal forming the electrode and of the anion. This can hardly be accounted for on the Ostwald-Nernst hypothesis. If the potential difference between Hg and KCl or KBr solutions be due to the amount of mercury as ion which has gone into solution, we must say that the amount varies as we change from KCl to KBr, or, in other words, that the negative ion has an effect. This is quite apart from the difficulty of accounting for the sign of the potential difference. I do not see that the relative solubilities of mercurous chloride and bromide can be dragged in to help out matters, because we do not have a saturated solution at all, and the difference in the electromotive forces is more likely to be connected with the difference of solubility as cause than as effect.

There are no experimental data, so far as I know, on potential differences at the contact surface of reversible electrodes except some

* This will not hold true till the concentration of the salt becomes zero; else we should get always the same potential difference, that of the metal in pure water, which is not the case. There will certainly be a minimum concentration beyond which the dissolved substance will not have the properties of matter in mass, and the potential difference will then be a function of the concentration.

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measurements by Neumann,* and these are not conclusive as regards the point that they were intended to prove, owing to an unfortunate choice of solutions. He measured the potential difference between thallium and solutions of thallium salts. Most of the salts were salts of organic acids, and Ostwald † had already found that when the negative ion was an organic radical its nature was immaterial. To settle this question one should take negative ions which show marked differences with non-reversible electrodes, such as chlorides, bromides, and iodides. As the negative ion has a very marked influence in these last named cases, and as there is no reason to suppose that the haloid salts form a class by themselves, the simplest assumption is that the negative ion always has an effect, and that in the cases where this does not appear, such as the organic radicals, we are measuring something else which is the same in all cases. Le Blanc ‡ found something similar in his studies of polarization, where beyond a certain point he obtained the value for the primary decomposition of water.

There are certain quantitative relations connected with the change of the negative ion which deserve to be brought out, and in Table XI. are given the most probable values for the potential differences of the

TABLE XI.

Solution.	Zn | Sol.	Cd | Sol.	Sol | Hg.
Chlorides . . .	0.589	0.255	0.562
Bromides . . .	0.507	0.174	0.483
Iodides	0.436	0.104	0.410

TABLE XII.

Solution.	Zn | Sol. | Hg.	Cd | Sol. | Hg.
Chlorides	1.151	0.817
Bromides	0.990	0.657
Iodides	0.846	0.514
Sulfates	1.302	0.969

* Zeitschr. f. ph. Ch., XIV. 225, 1894.
† Ibid., I. 605, 1887.
‡ Ibid., VIII. 315, 1891.

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TABLE XIII.

Solution.	Zn.	Cd.	Hg.
KCl – KBr . . .	0.082	0.081	–0.079
KBr – KI . . .	0.071	0.070	–0.073
KCl – KI . . .	0.153	0.150	–0.152

metals Hg, Zn, and Cd in solutions of chlorides, bromides, and iodides, while in Table XII. are the corresponding values for the single liquid, non-reversible cells with Zn and Hg, Cd and Hg, as electrodes.*

We notice that the numerical change in passing from a chloride to a bromide or iodide solution is the same for these three metals and that the sign is the same for zinc and cadmium, as is shown in Table XIII. This enables us to formulate matters a little more clearly. The potential difference between a metal and a salt solution is the sum of two terms, one due to the metal and the solvent, the other to the negative ion. For certain metals in certain solutions the term due to the negative ion is independent, numerically, of the nature of the metal considered. For instance, the potential differences Zn|KCl, Zn|KBr, Cd|KCl, Cd|KBr, Hg|KCl, and Hg|KBr will be $A+a$, $A+b$, $B+a$, $B+b$, $C-a$, and $C-b$. The electromotive forces of the cells Zn|KCl|Cd and Zn|KBr|Cd will be $E_1 = A+a-B-a$, and $E_2 = A+b-B-b$, whence we see that $E_1 = E_2$, which had already been found experimentally. For Zn|KCl|Hg and Zn|KBr|Hg we shall have $E_1 = A+a-C+a$ and $E_2 = A+b-C+b$, and E_1 will not be equal to E_2. By referring to Table III. we can now extend our generalization and make it more precise. With the metals Mg, Zn, Cd, Sn, Pb, and Bi in solutions of chlorides, bromides, iodides, sulphates, nitrates, acetates, carbonates, and oxalates, the term due to the negative ion is not a function of the electrode. There is not much doubt that the alkaline metals, the metals of the alkaline earths, and the metals of the iron group belong in this same series. Ostwald's measurements show that most organic acids may be added to the above list of solutions. With mercury the numerical value of the term due to the negative ion is the same as with the previous metals, but the sign is opposite. With platinum the numerical value is no longer

* There is certainly an error in the relative positions of Sn and Pb as given by my determinations, so I give no data for them in Table XII.

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the same. In which of these three groups copper, silver, gold, and the other metals belong, I cannot say, though silver is probably like mercury. The results in Tables XI.–XIII. open up a whole series of problems to be settled by future investigators. The values for the differences of the terms for any two negative ions have to be determined with accuracy; the behavior of the metals Cu, Ag, etc. must be examined. The work of Magnanini * shows that other relations hold when the dissolved salt is an oxidizing or reducing agent, and that the value Zn|RX|Cd, for instance, is not a function of the metals only, if RX is an oxidizing agent. It is also well known that in cases where the electrode metal cannot exist in the solution as ion that the general relations already pointed out do not hold. From the results of Negbaur † and of Jones ‡ we must conclude that the term which I have represented by A, B, C, etc., varies with the nature of the solvent. The amount of this variation is entirely unknown as yet, and it is equally impossible to say beforehand how a change in the solvent will affect the term due to the negative ion.

If we consider the cell $Zn|ZnCl_2|ZnBr_2|Zn$, the two solutions being assumed to be of the same concentration and dissociation, and the wandering velocity of the bromine ion being further assumed to be identical with that of the chlorine ion, we should expect an electromotive force of 0.080 volt. This has not been taken into account by Goodwin § in his determinations of the solubilities of silver chloride, bromide, and iodide. Goodwin determined the electromotive forces of the cells $Ag|AgNO_3|AgCl + KCl|Ag$, $Ag|AgNO_3|AgBr + KBr|Ag$, and $Ag|AgNO_3|AgI + KI|Ag$. From the observed electromotive forces the solubilities were calculated by the formula $s = \sqrt{\frac{p_1 p_2}{\varphi}}$, where $\log \varphi = \frac{E}{C}$. In this equation s is the solubility, p_1 the concentration of the Ag ions in the nitrate solutions, p_2 the concentration of the Cl, Br, or I ions in the corresponding solutions, E is the electromotive force of the cells, and C the integration constant, which is equal at 25° to 0.0256. It is more than probable that a cor-

* Rend. Acc. Linc., VI. 182, 1890.

† Wied. Ann., XLVII. 27, 1892.

‡ Zeitschr. f. ph. Ch., XIV. 346, 1894.

§ Zeitschr. f. ph. Ch., XIII. 645, 1894. It is only fair to Mr. Goodwin and to myself to say that I have pointed out to him privately the objections that I made to his results that he might correct them himself if he felt so inclined. He thinks that it would be better for me to make my comments in print, and I have accordingly done so.

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rection ought to be applied for a possible difference of log P in nitrate and chloride solutions; but as this value is not accurately determined I will first calculate the solubilities on the basis of the assumption that log P_{NO_3} = log P_{Cl}.* We find, from Table XIII.,

log P_{Cl} — log P_{Br} = 0.080, and log P_{Cl} — log P_I = 0.152 volt.

These values are to be subtracted from the electromotive forces observed with AgBr and AgI in order to get the term E called for by the formula. In Tables XIV.–XVI. I give the results of these calculations.

In the first column are the values for p_1; in the second, for p_2; in the third, the electromotive forces; in the fourth, the solubilities as calculated by Goodwin; in the fifth, the solubilities as calculated by myself under the assumption that log P_{NO_3} = log P_{Cl}: and in the sixth, the values if one assumes that log P_{NO_3} — log P_{Cl} = 0.03 volt. I also give the solubilities found by Kohlrausch and Rose,† and by Holleman ‡ with the conductivity method.

TABLE XIV.§

Conc. Ag Ions = p_1.	Conc. Cl Ions = p_2.	E. M. F.	Calc. S_1.	Calc. S_2.	Calc. S_3.
0.0813	0.0861	0.451	1.24×10^{-5}	1.25×10^{-5}	2.25×10^{-5}
0.0813	0.0861	0.449	1.28×10^{-5}	1.30×10^{-5}	2.34×10^{-5}
0.04295	0.04455	0.418	1.25×10^{-5}	1.25×10^{-5}	2.24×10^{-5}
0.04295	0.04455	0.419	1.23×10^{-5}	1.22×10^{-5}	2.20×10^{-5}
Solubility AgCl at 25°, average			1.25×10^{-5}	1.25×10^{-5}	2.26×10^{-5}
Kohlrausch and Rose			1.44×10^{-5}	at 25°	
Holleman			1.81×10^{-5}	at 25°	

It will be seen that the second column of solubilities agrees much better with the results obtained by other investigators than the solu-

* The term log P_{Cl} denotes the value of log P for the metal under discussion when in a chloride solution.

† Zeitschr. f. ph. Ch., XII. 324, 1893.

‡ Ibid., XII. 125.

§ S_1 and S_2 in this table should be identical, as they are calculated from the same data by the same formula; the variations are due to errors in calculation.

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TABLE XV.

Conc. Ag Ions $= p_2$.	Conc. Br Ions $= p_2$.	E. M. F.	Calc. S_1.	Calc. S_2.	Calc. S_3.
0.0813	0.0861	0.598	7.1×10^{-7}	33.8×10^{-7}	60.7×10^{-7}
0.0813	0.0861	0.603	6.4×10^{-7}	30.1×10^{-7}	55.0×10^{-7}
0.0813	0.0861	0.597	7.2×10^{-7}	34.4×10^{-7}	61.9×10^{-7}
0.04295	0.04455	0.570	6.4×10^{-7}	30.5×10^{-7}	54.9×10^{-7}
0.04295	0.04455	0.571	6.3×10^{-7}	29.9×10^{-7}	53.8×10^{-7}
0.04295	0.04455	0.570	6.4×10^{-7}	30.5×10^{-7}	54.9×10^{-7}
Solubility AgBr at 25°, average			6.6×10^{-7}	31.5×10^{-7}	56.9×10^{-7}
Kohlrausch and Rose			20.9×10^{-7}	at 25°	
Holleman			30.2×10^{-7}	at 25°	

TABLE XVI.

Conc. Ag Ions $= p_1$.	Conc. I Ions $= p_2$.	E. M. F.	Calc. S_1.	Calc. S_2.	Calc. S_3.
0.0813	0.0861	0.815	1.02×10^{-8}	19.9×10^{-8}	35.7×10^{-8}
0.0813	0.0861	0.813	1.06×10^{-8}	20.7×10^{-8}	37.2×10^{-8}
0.0813	0.0861	0.815	1.02×10^{-8}	19.9×10^{-8}	35.7×10^{-8}
0.04295	0.04455	0.787	0.94×10^{-8}	18.0×10^{-8}	32.3×10^{-8}
0.04295	0.04455	0.786	0.96×10^{-8}	18.3×10^{-8}	32.9×10^{-8}
0.04295	0.04455	0.790	0.88×10^{-8}	17.0×10^{-8}	30.5×10^{-8}
Solubility AgI at 25°, average			0.98×10^{-8}	19.0×10^{-8}	34.0×10^{-8}
Kohlrausch and Rose			60.0×10^{-8}	at 18°	
Holleman			395.0×10^{-8}	at 28.4°	

bilities calculated by Goodwin. The solubilities in the last column do not show as good an agreement; but I do not feel sure that this proves that the formula by which they are calculated is wrong. It seems to me quite as probable that these figures represent the actual solubilities in the cells examined by Goodwin; but not the real solubilities of

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AgCl, AgBr, AgI. The solubilities of AgCl and AgBr are much changed by continued shaking,* and I cannot find that Goodwin has taken this into account at all. I conclude, therefore, that if he had shaken his AgCl and AgBr he would have found much smaller electromotive forces than those recorded in his paper. He has tried to prove the accuracy of his formula in two ways. Having calculated the solubilities by substituting the experimental data for the electromotive forces in the formula, he reverses the operation, and, substituting the solubilities, he calculates the electromotive forces. It is true that there is an intervening step, but the principle is the same, also the result. If he had taken the cells $Ag|AgNO_3|AgCl + KCl|Ag$, and $Ag|AgNO_3|AgBr + KBr|Ag$, and substituted directly in these, the fallacy of such a test would have been patent. Instead of this he has combined the two cells

$$Ag|AgCl + KCl|AgNO_3|Ag|AgNO_3|AgBr + KBr|Ag =$$
$$Ag|AgCl + KCl|AgBr + KBr|Ag,$$

calculated the electromotive force of the resultant cell, and compared this with the experimental value and with the difference of the mean of the two component cells. Any other formula, which had given fairly constant values for the solubilities, would have stood the test equally satisfactorily. If, instead of taking Goodwin's formula and his value for AgBr, 6.6×10^{-7} reacting weights per litre, one takes, for instance, my first modification of his formula and the corresponding value for AgBr, 31.5×10^{-7} units, one will reproduce his table exactly. One cannot agree with him when he says, in regard to this table: "Die Uebereinstimmung der beobachteten mit den berechneten Werten ist eine sehr gute, wie dem ja nicht anders sein konnte, wenn die frühere Formel (25), nach der die Löslichkeiten berechnet wurden, überhaupt richtig war. Sie bestätigt also diese Formel." † The other proof is not satisfactory in the light of my experiments. Goodwin determined the solubility of thallium bromide by the electrical and by the analytical methods, the difference between the two being about 10 per cent of the total solubility. This result cannot be compared with the experiments on the solubilities of the silver haloids, because the conditions were not the same. In the thallium determinations the cell used was of the form $Tl|TlBr + KNO_3|TlBr + KBr|Tl$. There were bromine ions in contact with both electrodes, while with the silver salts the bromine ions only came in contact with one electrode.

* These Proceedings, XXX. 385, 1894.

† Zeitschr. f. ph. Ch., XIII. 651, 1894.

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One other point remains to be considered, whether the potential difference at the surface of a reversible electrode is a function of the concentration at all. The only direct measurements are those of Neumann,* which confirm the Nernst theory in every detail. In addition, there are many determinations on two-liquid cells made chiefly by Ostwald's pupils, and in all these instances there is a most satisfactory agreement between the theory and the facts. On the other hand, there are a few observations by different people which are not so easily reconciled with the theory. In Table XVII. I give some measurements of Paschen's † on cells having zinc and mercury electrodes and solutions of $ZnSO_4$ and $MgSO_4$ of varying concentrations as electrolyte. The first column gives the nature of the cell; the second, the specific gravity of the electrolyte; the third, the concentration in grams per hundred grams of the solution; the fourth, the electromotive force observed. The values for the concentrations are only approximate, because they were not determined by Paschen directly, and I have taken them from Landolt and Börnstein's tables.

TABLE XVII.

Electrodes.	Electrolyte.	Density.	% in g.	E. M. F.
ZnHg	$MgSO_4$	1.042	4.	1.194
ZnHg	$MgSO_4$	1.040	4.	1.236
ZnHg	$MgSO_4$	1.040	4.	1.186
ZnHg	$ZnSO_4$	1.433	32.9	1.249
ZnHg	$ZnSO_4$	1.409	31.5	1.252
ZnHg	$ZnSO_4$	1.403	31.1	1.309
ZnHg	$ZnSO_4$	1.402	31.1	1.327
ZnHg	$ZnSO_4$	1.400	31.0	1.236
ZnHg	$ZnSO_4$	1.315	25.5	1.310
ZnHg	$ZnSO_4$	1.305	2.50	1.238

These figures lose a good deal of their value owing to the considerable variation in the determinations for the same solutions, and because

* Zeitschr. f. ph. Ch., XIV. 225, 1894. † Wied. Ann., XLIII. 570, 1891.

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the range of concentrations is too limited; but two things are very noticeable in spite of this. In the cell $Zn|ZnSO_4|Hg$ the electromotive force does not decrease with increasing concentration of zinc sulphate, as it should according to the theory. The cells $Zn|MgSO_4|Hg$ have the same value as the cell $Zn|ZnSO_4|Hg$ or a smaller one, while the theory demands a larger one. The same thing is seen, though in a less satisfactory manner, in the experiments of Damien.* He used zinc and copper as electrodes, and his results are given in Table XVIII. The first column shows the electrolyte; the second, the specific gravity of the solution; the third, the percentage composition; the fourth, the electromotive force when ordinary zinc was used; the fifth, the corresponding value when the electrode was amalgamated.

TABLE XVIII.†

ZnCu Electrodes.

Electrolyte.	Sp. gr. at 15°.	% in g.	E. M. F.	Amalg. Zn. E. M. F.
K_2SO_4	1.036	4.5	1.035	1.067
Na_2SO_4	1.038	10.*	1.012	1.037
$(NH_4)_2SO_4$	1.075	13.1	1.012	1.019
$MgSO_4$	1.035	5.8*	1.047	1.059
$Al_2(SO_4)_3$	1.135	5.8	1.050	1.062
$ZnSO_4$	1.064	9.2*	1.004	1.047.
KCl	1.077	12.0	0.788	0.802
NaCl	1.061	8.5	0.805	0.810
NH_4Cl	1.039	13.	0.845	0.850
$BaCl_2$	1.110	12.	0.782	0.820
$CaCl_2$	1.212	23.	0.743	0.741
$ZnCl_2$	1.384	37.5	0.746	0.752

As will be noticed, there are marked variations even in cases in which no one claims that there should be any, such as between ammo-

* Ann. Chim. Phys., [6.], VI. 289, 1885. The refererence to Vol. V. in Wied. Elektricität, I. 734, also in Beibl., X. 185, is a misprint.

† Stars refer to hydrated salt.

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nium sulphate and potassium sulphate solutions, between calcium chloride and ammonium chloride. This weakens the conclusions which one would like to draw from these experiments; but, making allowance for a large experimental error, it is very curious that $Zn|ZnSO_4|Hg$ should give so nearly the same value as the cells with indifferent sulphates, and that zinc chloride should be indistinguishable electrically from calcium chloride. The experiments of Hockin and Taylor * may be interpreted either way. They found that the combination of zinc and another metal in sulphuric acid gave a higher electromotive force than the same two metals in a saturated solution of zinc sulphate. This is not so convincing as if they had used potassium sulphate instead of sulphuric acid, because in all except dilute solutions free acids do give a higher value than the corresponding salts. The reason for this variation is unknown. When it comes to the absolute values in the zinc sulphate solution, matters are no better. With some of the metals, notably cadmium and mercury, the zinc sulphate appears to give the same value as any other sulphate; with others, there is qualitative agreement with Nernst's theory. The same remarks hold true of the work of Lindeck.† I have not access to the original paper of Wolff, and the review of it ‡ is too meagre to be of much assistance. He investigated, among other things, the effect of changing the concentration of the zinc sulphate in a one-liquid cell. His results are given in Table XIX. The first column shows the electrodes and the electrolyte; the second, the concentrations of the latter in specific gravities; the third, the corresponding electromotive forces.

In all cases there is a qualitative agreement with the theory; that is, the electromotive force increases with decreasing concentration of zinc sulphate. The quantitative agreement is not so satisfactory. In the second, third, sixth, and last cells given in the table, the variations are much too small, while in the other cases they are too large. The ratio of the strongest solutions to the weakest in the experiments of Wolff lies between 100 and 1000 to 1, which corresponds to a change of electromotive force of 0.05–0.09 volt owing to the bivalence of zinc. Some experiments which I made with the cell $Cd|CdCl_2|Hg$, the strength of the solution being unknown, gave me 0.815, 0.821, 0.814, average 0.817 volt, the same value which I had already found for the KCl solution.

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* J. Tel. Eng., VIII. 282, 1879.

† Wied. Ann., XXXV. 311, 1888.

‡ Beibl., XII. 700, 1888.

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TABLE XIX.

Cells	Densities.	E. M. F.
$Zn\|ZnSO_4\|Cu$	1.438 – 1.001	0.965 – 1.066
$Zn\|ZnSO_4\|CuO$	1.427 – 1.003	1.008 – 1.015
$Zn\|ZnSO_4\|Fe$	1.427 – 1.003	0.378 – 0.385
$Zn\|ZnSO_4\|Pb$	1.427 – 1.003	0.456 – 0.587
$Zn\|ZnCl_2\|Cu$	1.637 – 1.003	0.734 – 0.930
$Zn\|ZnCl_2\|Fe$	1.917 – 1.003	0.385 – 0.390
$Zn\|Zn(NO_3)_2\|Cu$	1.496 – 1.004	0.669 – 0.698

The simplest way to decide what effect the concentration of the reversible ion, if I may use such a phrase, has on the electromotive force, would be to make a series of measurements on reversible electrodes by the dropping-mercury method. I have not been in a position to do this, and I have had to find an easier, though less satisfactory, manner of settling the question. Suppose we have electrodes of zinc and copper in a mixture of zinc and copper sulphates, one solution. Increasing the concentration of the zinc sulphate or decreasing the concentration of the copper sulphate must diminish the electromotive force of the cell, and *vice versa* if the reverse operations be performed. Through the courtesy of Professors Trowbridge and Peirce of the Physical Laboratory, I have been able to make the few experiments necessary. As it was only required to find out whether there was any change at all, there was no need of determining the absolute value of the electromotive force. This made the experimental part very easy. I connected the cell with a large external resistance and a galvanometer. I changed the ratio of the two components in the solution, and noted the position of the galvanometer needle. I made measurements with the electrodes in pure zinc sulphate solutions, in pure copper sulphate solutions, and in mixtures of the two in varying proportions. Under all these different conditions I obtained the same electromotive force, showing that it is a function neither of the relative nor of the absolute concentrations.* Although one obtains the same value from

* This applies only to electrodes reversible in respect to the kation. I hope to make the case of electrodes reversible in respect to the anion the subject of a

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the different solutions, they do not behave exactly alike. With solutions of pure copper sulphate, or from mixtures containing copper sulphate in any quantity, the maximum value is obtained at once, and is very constant. With solutions of pure zinc sulphate or mixtures containing only traces of copper sulphate, the maximum value can be obtained only by vigorous stirring, and is very inconstant. There is, of course, nothing surprising about this, as it is what one would have predicted. It is a very striking and curious fact, that the Nernst formula, though deduced from apparently erroneous assumptions, should yet give the effect of changes of concentration in a two-liquid cell with such surprising accuracy.

It will be noticed that the electromotive forces of the non-reversible cells have nothing to do with the heats of reaction. This has always been known; but it acquires new significance since it has been shown that the non-reversible cells are to be considered, as far as the electromotive force is concerned, as limiting cases of the reversible two-liquid cells. In the cell $Zn|H_2SO_4|Ag$ there is not much doubt what reaction takes place; but it has nothing to do with determining the electromotive force. An interesting example of this, which also brings up another point, is the cell $Cu|CuSO_4|Pt$. Here the reaction consists in the replacement of copper by copper. What happens experimentally, on closing the circuit, is that copper is dissolved from the copper electrode and precipitated on the platinum until this latter becomes, electrically considered, an electrode of pure copper, when further action becomes impossible. Overbeck* made some experiments a few years ago to determine what thickness of copper made a platinum electrode behave like a piece of pure copper. His method was to deposit copper on platinum electrolytically, and was open to the objection that it was almost impossible to be certain that the copper was deposited uniformly over the surface of the platinum. By using the cell $Cu|CuSO_4|Pt$, it would seem that this difficulty might be avoided, as the plating is stopped automatically as soon as the minimum thickness is reached. Suppose now we balance this cell, to some extent, by an electromotive force less than its own. There will still be a tendency for copper to be deposited on the platinum; but it cannot be deposited to the thickness corresponding to pure copper, as it must then dissolve

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special communication. Since this paper was written there has appeared an article by G. Meyer, Wied. Ann., LIII. 848, 1894, which confirms my views, though with certain exceptions.

* Wied. Ann., XXXI. 337, 1887.

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up again under the influence of the external electromotive force. It can precipitate only till equilibrium is reached, and we shall have the condition referred to by Gibbs,* of a substance present in too small quantities to have the properties of "matter in mass." By making the external electromotive force differ infinitely little from the electromotive force of the cell, it would be possible, theoretically at any rate, to obtain an infinitely thin film of copper. It is to the separation of the ion on the electrode in such small quantities as not to have the properties of matter in mass that is due the gradual change of the polarization, instead of having a sudden change from the initial to the final value.

The main results of this research may be summed up as follows: —

1. The potential difference between a metal and an electrolyte is not a function of the concentration of the salt solution, nor of the nature of the positive ion, except in certain special cases.

2. It is a function of the electrode, of the negative ion, and of the solvent.

3. In aqueous solutions the potential difference is the sum of the term due to the electrode and the term due to the negative ion in the normal cases.

4. For most metals in most electrolytes the term due to the negative ion has the same numerical value and the same sign.

5. For mercury it has the same numerical value, but the opposite sign; for platinum, neither the same numerical value nor the same sign.

6. For platinum in a haloid solution the change of the electromotive force with the concentration is given by the formula

$$E_1 - E_2 = \tfrac{1}{2} RT \text{ nat. log } \frac{C_1}{C_2}$$

if the salt dissociates into three ions; by the formula

$$E_1 - E_2 = \tfrac{2}{3} RT \text{ nat. log } \frac{C_1}{C_2}$$

if it dissociates into two.

* Thermodynamische Studien, p. 393.

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VI.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

ON THE BEHAVIOR OF CERTAIN DERIVATIVES OF BENZOL CONTAINING HALOGENS.

By C. Loring Jackson and Sidney Calvert.

Presented May 9, 1894.

Introduction.

It is a well known fact that in substituted aromatic compounds the firmness with which atoms of halogen are attached to the benzol ring is diminished by the presence of nitro groups in certain positions, so that these atoms can be replaced by reagents, which would have no effect on them if the nitro groups had been absent. It has also been shown that certain other negative radicals exert a similar loosening effect: these are the two oxygen atoms in substituted quinones — chloranil and bromanil are very reactive bodies — the hydroxyl groups in phenols,* and especially in substituted resorcine,† and also probably carboxyl.‡ The object of the research described in the present paper was to determine whether such a loosening effect could be produced by less negative radicals, and for this purpose we have taken up the study of derivatives of benzol, in which the substituting radicals are halogens only, so that both the radicals removed and those which make the removal possible belong to this same class, and the latter are distinctly less negative than any of those enumerated above. The amount of work already done in this field is meagre. Balbiano § found that paradibrombenzol was converted into parabromphenetol, brombenzol, and a little benzol, when it was heated to 190° with sodic ethylate. The same substance with sodic methylate at 150° gave

* Armstrong and Harrow, Journ. Chem. Soc., 1886, p. 447.
† Jackson and Dunlap, These Proceedings, XXIX. 228.
‡ Rahlis, Ann. Chem., CXCVIII. 112.
§ Gazz. Chim., XI. 401.

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according to Blau * parabromphenol, parabromanisol, and a little hydroquinone dimethylether. Blau † also found that symmetrical tribrombenzol gave with sodic methylate at 130° symmetrical dibromphenol and the corresponding anisol as principal products. These results indicate that the atoms of bromine in these di-and tribrombenzols exert some loosening effect, as monobrombenzol must be heated to 200° before it reacts with sodic methylate; ‡ but all these actions take place in sealed tubes, and even the maximum difference between their temperatures of reaction and that of monobrombenzol is not very great, only 70°. We decided therefore, in taking up this subject, to try to obtain reactions in open vessels, that is, under conditions which would have prevented all action with monobrombenzol, and to do this it was obvious that we must increase the number of the atoms of halogen which are to produce the loosening effect. We selected for our first experiment accordingly the tribromiodbenzol having the constitution Br.H.Br.I.Br.H, as in this compound we have iodine as the element to be removed, and this is usually less strongly attached to the ring than bromine or chlorine, and the three atoms of bromine which are to produce the loosening effect are in the most favorable positions for this purpose (two ortho and one para). Trichloriodbenzol would probably have been even better, because chlorine is more negative than bromine, but we preferred the bromine compound on account of the great difficulty of preparing the trichloraniline in quantity.

Upon trying a variety of reagents with the unsymmetrical tribromiodbenzol, we obtained negative results with all except two, sodic ethylate and sodic methylate. These converted it into symmetrical tribrombenzol, melting point 119°, by replacing the iodine with hydrogen, the sodic ethylate acting to some extent even in the cold, more freely when the solution in alcohol and benzol was boiled under a return condenser, while the sodic methylate did not act in the cold, and only to a limited extent boiling. The unsymmetrical tetrabrombenzol Br.H.Br.Br.Br.H, which differs from the preceding compound only in having an atom of bromine in place of the iodine, was also partially converted into symmetrical tribrombenzol by boiling with sodic ethylate, but there was much less action than with the iodine compound, the tetrabrombenzol undergoing about as much substitution when the solution was boiling, as was the case with the tribromiodbenzol in the cold. The tribromchlorbenzol Br.H.Br.Cl.Br.H, on the other

* Monatsh. f. Chem., VII. 627. † Ibid., 630. ‡ Ibid., 636.

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hand, was entirely unaffected by a solution of sodic ethylate in open vessels. These experiments show that the presence of the three bromine atoms exercises a loosening effect similar to that exhibited by nitro groups, although much weaker in degree. They also furnish an additional case in which the stability of the aromatic compounds of the different halogens increases in the order iodine, bromine, chlorine. This is worth noting, because Körner * states that the halogens are removed from dinitrohalogenbenzols (X 1, NO_2 2, NO_2 4) in exactly the reverse order; that is, chlorine most and iodine least easily.

We next turned our attention to the tetrabrombenzol melting at 174°–175° which has been proved by work done in this Laboratory to have the symmetrical constitution Br.Br.H.Br.Br.H, as in this substance only two of the bromine atoms are in the positions to the one to be removed (ortho and para) which had proved effective in the unsymmetrical compound. This, however, did not affect the result materially, as this tetrabrombenzol was converted into unsymmetrical tribrombenzol (Br 1, Br 2, Br 4) by the boiling solution of sodic ethylate to about the same extent as the unsymmetrical tetrabrombenzol. In separating the small quantity of tribrombenzol formed from the large amount of unaltered tetrabrombenzol we have obtained excellent results in both the cases just mentioned by exposing the mixture for a long time to the lowest temperature at which anything sublimes. The sublimate thus obtained, if not the pure tribrombenzol, could be converted into it by a single repetition of this rough fractional sublimation.

An arrangement of the bromine atoms entirely different from the effective ortho para positions is found in the symmetrical tribrombenzol Br.H.Br.H.Br.H, as here all the halogen atoms are in the meta position to each other, but, as has been already mentioned, Blau found that one of the atoms of bromine was removed by the action of sodic methylate at 130°. As our work just described has shown that sodic ethylate is more active than the methylate, we thought this might act even in open vessels, and on trying the experiment have found that sodic ethylate in boiling alcoholic solution removes from symmetrical tribrombenzol a portion of its bromine. The organic products of the partial reaction were oily, but, as the object of our experiment was to determine whether a reaction took place, and not what its products were, no attempt was made to examine them. This is not the only

* Gazz. Chim., 1874, p. 323, note.

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case in which one of three radicals in the symmetrical position has been removed, as Lobry de Bruyn * has converted symmetrical trinitrobenzol into dinitranisol or dinitrophenetol by the action of the sodic alcoholates in open vessels. The work of Blau and Lobry de Bruyn, therefore, establishes this as a general behavior of symmetrical compounds, and such replacements are the more remarkable, because a single negative radical has no effect upon one other in the meta position.

In the work with unsymmetrical tetrabrombenzol, mentioned above, it was only the fourth atom of bromine (in the diortho para position to the others) that was replaced by hydrogen, but in some work upon the corresponding dinitro compound $C_6Br_4(NO_2)_2$, done some years ago by W. D. Bancroft and one of us, this atom of bromine remained obstinately unattacked when other atoms of bromine were removed; † in the same way the reduction of tetrabromdinitrobenzol with tin and hydrochloric acid gave monobromphenylene diamine,‡ so that in these cases the symmetrical atoms of bromine alone were removed, and the action was exactly the reverse of that obtained with tetrabrombenzol and sodic ethylate. This difference is explained by the facts that in the tetrabrombenzol the three atoms of bromine in the trimeta position are the loosening radicals, whereas in the tetrabromdinitrobenzol they are those which are loosened. In this connection we decided to try the action of sodic ethylate on tetrabromdinitrobenzol, as this experiment had not been included in the previous work of W. D. Bancroft and one of us, and we found that tetrabromdinitrobenzol ($Br.NO_2.Br.NO_2.Br.Br$) was converted by the action of a cold solution of sodic ethylate into the tribromnitroresorcine diethylether melting at 101°, and first obtained by W. H. Warren and one of us § by the action of sodic ethylate on tribromtrinitrobenzol. This substance has the formula $C_6Br_3NO_2(OC_2H_5)_2$, and must have been formed in this case by the replacement of one nitro group and the fourth atom of bromine by ethoxy groups, just as it was formed from the tribromtrinitrobenzol by the replacement of two nitro radicals by ethoxyls. If the action with the tetrabrom body is analogous to that with the trinitro compound, there should be formed at the same time by a parallel reaction a substituted phloroglucine, in this case dinitrobromphloroglucine or its ethers;

* Rec. d. Tr. Chim., IX. 208, XIII. 149.

† These Proceedings, XXIV. 288. Sodium malonic ester gave the compound $C_6HBr_2(NO_2)_2\,CH(COOC_2H_5)_2$; reduction of this gave bromamidoxindol; aniline gave $C_6Br(NO_2)_2\,(C_6H_5NH)_3$.

‡ See the following paper.

§ These Proceedings, XXV. 183.

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but although we have found indications that such a substance is formed, we have not succeeded in isolating it.

The principles governing the replacement of radicals attached to the benzol ring, which we have brought forward in this introduction, make it possible to explain the strange behavior of tribromtrinitrobenzol with sodic ethylate. This action consists in the two following reactions, which take place side by side.*

$$C_6Br_3(NO_2)_3 + 3\ C_2H_5ONa = C_6(OC_2H_5)_3(NO_2)_3 + 3\ NaBr.$$

$$C_6Br_3(NO_2)_3 + 2\ C_2H_5ONa = C_6Br_3NO_2(OC_2H_5)_2 + 2\ NaNO_2.$$

In this substance we seem to have two zones of action, one consisting of the three symmetrically disposed bromine atoms, the other of the three nitro groups also symmetrically disposed, and the action in each molecule is confined to one of these zones, if it is carried on in the cold. In the first or bromine zone the atoms of bromine are submitted to two loosening influences: (*a*) that of the three nitro groups in the diortho and para positions to each bromine atom, and (*b*) that of the trimeta bromine atoms on each other. In the second or nitro zone also we have two loosening influences: (*c*) that of the three bromine atoms diortho and para to each nitro group, and (*d*) the loosening effect of the three symmetrical nitro groups on each other. Of these loosening influences (*a*) is by far the strongest, and (*b*) the weakest; it seems therefore that the combined effect of (*c*) and (*d*), of intermediate strength, is about equal to that of (*a*) and (*b*) together; consequently each of these zones of action lies about equally open to the attack of the sodic ethylate, and the two reactions take place simultaneously. When the solvent is alcohol alone, they run to about the same extent. If the repellent action of the three symmetrical nitro groups (*d*) is removed, that is, if tribromdinitrobenzol is used instead of the trinitro body, the nitro groups should be much less loosened than the bromine atoms, and as a matter of fact there has been observed in this case no tendency to remove the nitro groups, the action being confined to the bromine zone, causing the formation of $C_6Br(OC_2H_5)_2(NO_2)_2H$, or $C_6H(OC_2H_5)_2(NO_2)_2H$.

The work described in this paper has furnished us with three additional cases, in which atoms of halogens have been replaced by hydro-

* These Proceedings, XXVII. 283. Tetrabromdinitrobenzol acts in the same way, as just stated, but for the sake of simplicity of expression the explanation has been confined to the trinitro body, although it applies equally well to the tetrabrom compound.

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gen under the action of sodic ethylate, but even with these we do not feel that enough facts are known to make it possible to deduce a general rule in regard to the conditions, which produce this curious reaction. The collection of such facts will be continued in this Laboratory.

We also tried the action of fuming nitric acid on unsymmetrical tribromiodbenzol, and found that iodine was set free, and the organic product was the tribromdinitrobenzol melting at 192°, and having the constitution Br.NO_2.Br.NO_2.Br.H.

A few statistics which we have collected about the removal of radicals from substituted benzols may be given here. By far the greater number of such removals are those in which a negative radical stands in the ortho position to the radical removed. Of these we have counted over sixty cases, in only nine of which the negative radical is a halogen. Of the cases of removal, where there is no negative radical in the ortho position, we have found four in which a negative radical is in the para position to the radical removed; these are $C_6H_4Br_2$, $C_6H_4ClNO_2$, $C_6H_4BrNO_2$, and $C_6H_4(NO_2)_2$; and to these perhaps should be added five of the nine cases mentioned above, in which the ortho radical is a halogen, as in all of these there is a nitro group in the para position to the radical removed.* In no case is a radical removed which is only in the meta position to a single negative radical; † but if there are two negative radicals in meta positions to the radical attached (symmetrical tri-compound), there are two cases in which substitution has been observed, $C_6H_3Br_3$ and $C_6H_3(NO_2)_3$.

Experimental Part.

Behavior of Tribromiodbenzol.

The tribromiodbenzol (I 1, Br 2, Br 4, Br 6) was made from symmetrical tribromaniline by replacing the amido group by an atom of iodine. Silberstein,‡ who discovered this substance, made it from the nitrate of diazotribrombenzol. We have preferred to use the sulphate, and, as our method seemed to give a better result than Silberstein's

* In the other cases where a radical was removed, which was ortho only to halogens, these halogens were in the diortho position, and therefore probably were sufficient to cause the removal.

† The conversions of meta and para nitranisol into the corresponding nitranilines were not counted, because they took place at such a high temperature, 200°; but perhaps they should be added to the list given above.

‡ Journ. Prakt. Chem., [2.], XXVII. 119.

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to judge from his statement, we give it in detail. Ten grams of symmetrical tribromaniline were mixed with moderately dilute sulphuric acid in such proportion that there was one molecule of the acid to each molecule of the tribromaniline; the calculated amount of solid sodic nitrite was then added in small quantities at a time, shaking the loosely corked flask after each addition until the red fumes were absorbed. The mixture after standing over night was filtered, and then treated with hydriodic acid till there was no further action. The slightly brown precipitate was washed with water, and purified by crystallization from a mixture of benzol and alcohol, when it showed a melting point of 104°. Silberstein gives 103°.5. For greater safety it was analyzed, with the following result.

0.3374 gram of the substance gave 0.6119 gram of a mixture of argentic bromide and iodide.

	Calculated for $C_6H_2Br_3I$.	Found.
Iodine and Bromine	83.24	83.32

We find the solubilities of the substance the same as those given by Silberstein, but we do not agree with him when he says it sublimes easily, as we have found that it sublimes much less easily than symmetrical tribrombenzol.

To study the action of sodic ethylate on tribromiodbenzol, 6 grams of it were dissolved in anhydrous benzol, and mixed with 40 c.c. of an alcoholic solution of sodic ethylate, containing 2 grams of sodium, that is, more than enough to remove all the halogen atoms present. The mixture was then heated on the steam bath under a return condenser for one hour, when the liquid had taken on a dark color, and a brownish precipitate had appeared; the liquid was now evaporated, and the residue treated for half an hour with a large quantity of water, filtered, and washed, when it weighed 4.1 grams. Upon subliming this residue, 2 grams of sublimate were obtained in small white needles which melted at 119°–120°, the melting point of symmetrical tribrombenzol. An analysis of the sublimate gave the following result.

0.2612 gram of the substance gave by the method of Carius 0.4695 gram of argentic bromide.

	Calculated for $C_6H_3Br_3$.	Found.
Bromine	76.18	76.51

There can be no doubt, therefore, that the substance is tribrombenzol, formed by the replacement of the atom of iodine in the tribrom-

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iodbenzol by hydrogen. The residue which did not sublime was a brownish yellow powder, containing many black specks. It did not melt at 300°, but melted with blackening when held over the free flame. It was not completely soluble in any of the common solvents, and all our efforts to obtain from it a body fit for analysis have proved fruitless.

The experiment was next repeated under the same conditions, except that the mixture was not heated, but allowed to stand three days at the ordinary temperature. At the end of this time it had turned dark brown, in fact a pale brown color appeared almost as soon as the materials were mixed; the solvents were then allowed to evaporate spontaneously, and the residue treated with water as in the previous experiment, when the aqueous filtrate gave a strong test with starch paste and chlorine water for iodine. The residue insoluble in water was sublimed at a very gentle heat, and crystals of symmetrical tribrombenzol were obtained recognized by their melting point, 119°–120°. The residue, which did not sublime at this gentle heat, was crystalline and of a reddish white color, very different from the amorphous brown product obtained under the same conditions from the action of hot sodic ethylate. This crystalline residue after three recrystallizations from a mixture of benzol and alcohol showed the melting point 104°, and was therefore unaltered tribromiodbenzol. It seems, therefore, that cold sodic ethylate behaves like hot, but the action is less complete. An alcoholic solution of sodic hydrate, after being warmed for ten minutes with a solution of tribromiodbenzol in benzol, converted it into tribrombenzol with elimination of iodine. This, therefore, acted in the same way as the hot solution of sodic ethylate, but the yield seemed to be larger, and the residue from the sublimation was lighter in color (yellow) and free from black specks. It did not, however, prove to be more manageable than that previously obtained. These differences may be due to the shorter heating, ten minutes in this case instead of one hour when the ethylate was used. Several attempts were made to detect the aldehyd, which it seemed probable was formed as the secondary product in the replacement of the iodine by hydrogen, but these led to no definite result.

Sodic methylate when boiled with a benzol solution of tribromiodbenzol for over an hour gives a result similar to that obtained from cold sodic ethylate; that is, tribrombenzol was formed, but there was a large amount of undecomposed tribromiodbenzol. The two substances were separated by careful sublimation, and recognized by their melting points. Cold sodic methylate, on the other hand, gave no

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action even after standing three days. This was proved by testing the aqueous washings for halogens with negative results, and recovering essentially all of the tribromiodbenzol used.

The following reagents had no effect on the tribromiodbenzol: sodic phenylate in alcoholic solution boiling, sodic hydrate in aqueous solution boiling, sodic carbonate in aqueous solution boiling, zincic oxide and water in a sealed tube at 200° for twelve hours, argentic acetate in aqueous solution boiling, aniline boiling, tin and hydrochloric acid, sodium malonic ester both cold and hot. The proof that no action had taken place in these experiments was obtained either by the recovery of the unaltered tribromiodbenzol, or by tests for a salt of the halogens which gave negative results. In most cases both methods of proof were applied.

To determine whether the removal of the iodine was due to the loosening effect of the three atoms of bromine or to the slight attraction of iodine alone for carbon, iodbenzol was treated with sodic ethylate under the same conditions which had produced an action on the tribromiodbenzol; but after heating the mixture for an hour and a half no test for sodic iodide could be obtained, showing that there had been no action.

Action of Fuming Nitric Acid on Tribromiodbenzol.

When tribromiodbenzol was treated with fuming nitric acid, it lost its white crystalline appearance even in the cold, and became converted into a yellow powder. If the mixture was allowed to stand at ordinary temperatures over night, and then water added to it, iodine appeared both in scales and in the form of vapor, as a great amount of heat was given off. The identity of the iodine was also established by the smell and the violet color of its solution in carbonic disulphide. If now the insoluble portion was washed with cold alcohol until free from iodine, and then recrystallized several times from a mixture of benzol and alcohol, it showed the constant melting point 191°, which indicated that the substance was tribromdinitrobenzol, and this was confirmed by the following analysis.

0.3375 gram of the substance gave by the method of Carius 0.4740 gram of argentic bromide.

	Calculated for $C_6HBr_3(NO_2)_2$.	Found.
Bromine	59.26	59.78

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The somewhat high result may be due to a trace of a substance containing iodine. If the mixture of tribromiodbenzol and fuming nitric acid was boiled, the organic product was the same, but no free iodine was obtained.

Behavior of Unsymmetrical Tetrabrombenzol melting at 98°.

The action of sodic ethylate on this substance was selected for study, because that reagent had given the best results in the work on tribromiodbenzol just described. To prepare the unsymmetrical tetrabrombenzol, 20 grams of tribromaniline were dissolved in 180 c.c. of hot glacial acetic acid, about 80 c.c., that is a considerable excess, of a distilled solution of hydrobromic acid (boiling point 125°) added, and, disregarding any precipitate formed, the mixture treated with sodic nitrite in the proportion of a molecule and a half or two molecules to each molecule of the tribromaniline. For this purpose the finely powdered nitrite was slowly sifted with vigorous stirring into the solution, which had previously been cooled so that it felt barely warm to the hand. The white crystals which were suspended in it gradually changed into a dirty brown solid, much of which dissolved even in the cold. The mixture was then heated for two or three hours on the water bath; the solid matter at first went into solution, but later the tetrabrombenzol, as it formed, separated, principally in long white needles, or sometimes in part as a semiliquid brown mass. The needles were separated mechanically, and were usually found to be pure. The semiliquid portion solidified in a short time, and was purified by dissolving it in a little hot benzol, and pouring this solution into alcohol. The tetrabrombenzol precipitated in this way had a slight reddish color, while the mother liquor was of a dark claret-red. The precipitate was easily obtained white by one or two recrystallizations from a large volume of alcohol, to which it was well to add a little benzol. In this way 20 grams of the tribromaniline gave 22 grams of tetrabrombenzol, instead of the 23.88 grams required by the theory, a yield of 92 per cent.

Eight grams of the tetrabrombenzol were mixed with an alcoholic solution of sodic ethylate, made from 2 grams of sodium and 50 c.c. of absolute alcohol, and a little benzol to assist the solution of the tetrabrombenzol. The mixture was heated to boiling under a reverse condenser for two days, when it had taken on a blackish green color; it was then evaporated to dryness, and washed with water. The wash waters gave a good test for sodic bromide. The residue insoluble in water was sublimed at the lowest possible temperature, when a

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small amount of white needles was obtained, which melted at 119°, the melting point of symmetrical tribrombenzol. The residue which had not sublimed at the very low temperature used made up the principal bulk of the product, and was chiefly unaltered tetrabrombenzol. This method of fractional sublimation has also yielded us excellent results in another similar case, which will be described later in this paper. The sodic ethylate therefore acts on the tetrabrombenzol in the same way that it does on the tribromiodbenzol, replacing by hydrogen the bromine atom occupying the same position as the atom of iodine, but the action takes place with more difficulty, and is less complete.

Behavior of Unsymmetrical Tribromchlorbenzol.

The tribromchlorbenzol was prepared by a method similar to that used for the tetrabrombenzol. Upon adding the hydrochloric acid to the solution of tribromaniline in glacial acetic acid a precipitate of the chloride was formed, but this went into solution as the amido was converted into the diazo compound. Twenty grams of tribromaniline yielded 15 grams of tribromchlorbenzol melting at 82°. Two grams of this substance were heated for four hours with an alcoholic solution of sodic ethylate, prepared from half a gram of metallic sodium; when upon evaporation to dryness and washing with water only a very faint test for halogens could be obtained from the wash water, and the residue, which consisted of unaltered tribromchlorbenzol, weighed nearly 2 grams. A similar experiment with the tetrabrombenzol, in which the mixture was boiled for only three hours, gave a strong test for sodic bromide and a small amount of tribrombenzol. The chlortribrombenzol, therefore, if affected at all by sodic ethylate, is much less susceptible to its action than either the corresponding iod or brom compound.

Behavior of Symmetrical Tetrabrombenzol.

Tetrabrombenzol, melting at 174°–175°, which has been proved by work done in this Laboratory to have the symmetrical constitution (1, 2, 4, 5), was boiled for over twelve hours with an alcoholic solution of sodic ethylate; the brown liquid thus obtained, with some long rather dark colored crystals, which were deposited as it cooled, was evaporated to dryness, and the residue washed with water. The wash waters gave a good test for sodic bromide. The residue insoluble in water was then extracted, with a mixture of alcohol and benzol, filtered to remove a brown insoluble substance, and the filtrate concen-

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trated, when it deposited crystals which melted at 174°–175°, and were therefore the unaltered tetrabrombenzol. The mother liquor was evaporated to dryness, and cautiously sublimed at as low a temperature as possible; the crude sublimate melted at 42°–43°, and upon resubliming it with the same care its melting point rose to 44°, the melting point of unsymmetrical tribrombenzol (1. 2, 4), which must be formed if one of the atoms of bromine is removed from this tetrabrombenzol. Only a small portion of the substance, however, reacts with the sodic ethylate, by far the greater part remaining unaltered.

Experiment with Symmetrical Tribrombenzol.

Blau* states that tribrombenzol is converted by sodic methylate into symmetrical dibromphenol, when the substances are heated together in methyl alcohol solution for two to three days at 120°–130°. We accordingly tried an experiment to see whether sodic ethylate would have a similar action in open vessels, as we had used this reagent in the preceding work. Ten grams of tribrombenzol were boiled with a solution of the necessary amount of sodic ethylate in about 200 c.c. of alcohol for somewhat more than seventy hours; the aqueous wash waters from the product gave a good test for sodic bromide, and in addition to a large amount of unaltered tribrombenzol we obtained a very little of an oil, probably the dibromphenol ethylether, which is a liquid. As this result, which it will be observed confirms Blau, had given us all the information about the reaction which we wished, we did not pursue the work further.

Hexabrombenzol gave when boiled with sodic ethylate a good test for sodic bromide. The organic product was an oil, and a great deal of unaltered hexabrombenzol was recovered. Hexachlorbenzol gave a similar result.

Action of Sodic Ethylate on Tetrabromdinitrobenzol.

In the experiments described in this paper the fourth atom of bromine was removed from tetrabrombenzol by sodic ethylate, while in the work by W. D. Bancroft and one of us † upon the tetrabromdinitrobenzol, this fourth atom of bromine was not removed by aniline or sodium malonic ester. It seemed of interest therefore to try the tetrabromdinitrobenzol with sodic ethylate. and see whether it behaved like the tetrabrombenzol with this reagent or in the same way

* Monatsh. f. Chem., VII. 630. † These Proceedings, XXIV. 288.

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that it had behaved with the other reagents mentioned above. For this purpose 10 grams of tetrabromdinitrobenzol were dissolved in benzol, and treated with an alcoholic solution of the sodic ethylate made from 2 grams of sodium. The solution became claret-colored as soon as the sodic ethylate was added, but this color changed later to a reddish brown. There was no perceptible evolution of heat. The mixture was allowed to stand at ordinary temperatures for two days, after which it was evaporated spontaneously. The residue, after being washed with water, was recrystallized from alcohol until it showed the constant melting point 100° to 101°. This showed that it must be the tribromnitroresorcine diethylether made by Warren and one of us * from tribromtrinitrobenzol. This substance must have been formed by the replacement of one nitro group, and the fourth atom of bromine by two ethoxy radicals. To confirm this the wash waters of the original product were tested for a bromide and a nitrite, and good results obtained in both cases. If in this case the reaction has run as with tribromtrinitrobenzol,† which we should infer from the isolation of tribromnitroresorcine diethylether, the secondary product should be bromdinitrophloroglucine, or its ethers. As a matter of fact, an oil having the properties of a phenol was obtained by acidifying the aqueous wash waters from the first product of the reaction, but all our attempts to bring it into a form fit for analysis have failed, and we have been prevented from continuing work on this substance by the departure of one of us from Cambridge.

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* These Proceedings, XXV. 183. † Ibid., XXVII. 283.

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VII.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

BROMINE DERIVATIVES OF METAPHENYLENE DIAMINE.

By C. Loring Jackson and Sidney Calvert.

Presented May 9, 1894.

Introduction.

In the course of an extended investigation of the behavior of the tribromdinitrobenzol melting at 192°, carried on now for some years in this laboratory, we took up the reduction of this substance with tin and hydrochloric acid, since, if the bromine was not removed, new bromine derivatives of metaphenylene diamine must be obtained, or, on the other hand, the replacement of the bromine by hydrogen would be of interest, because cases in which a halogen is removed from the benzol ring under these conditions, are far from common. As, however, two of those already observed had occurred in the work on derivatives of tribromdinitrobenzol done in this laboratory, we had reason to hope that the proposed experiments might furnish us with an additional case, and contribute something toward determining the conditions under which this replacement of bromine by hydrogen takes place. After we had begun our work there appeared a paper * by Schlieper on the removal of bromine from aromatic compounds by tin and hydrochloric acid, in which he announced his intention of making an extended research in this field; we accordingly wrote to Victor Meyer, under whose direction Schlieper was working, asking if we might finish our work, and he has with great courtesy given us permission to do so.

We have succeeded in finding only the following cases in which bromine is replaced by hydrogen in aromatic compounds by reduction with tin and hydrochloric acid. Unsymmetrical brommetadinitrobenzol gives metaphenylene diamine.† Tribromdinitrobenzol sulphonic acid

* Ber. d. ch. G. XXV. 552.

† Zincke and Sintenis. Ber. d. ch. G., V. 792.

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gives bromdiamidobenzolsulphonic acid.* Dibromdinitrophenylmalonic ester gives bromamidoxindol.† nitrite of bromdinitrophenylmalonic ester gives amidoxyoxindol.‡ Bromnitrophenol gives amidophenol, and bromnitranisol gives amidoanisol.§ Metabromorthonitrobenzoic acid and its isomeric form both give anthranilic acid,‖ and Hübner¶ also states that he obtained small quantities of orthophenylene diamine from nitroparabromaniline, but that the principal product was the bromphenylene diamine; this, however, seems to be the only case observed, and none are recorded to our knowledge in the para series. We could find no record of the removal of other halogens under these conditions, until Schlieper published a second paper** (after our work on tribromdinitrobenzol was finished), in which he describes the reduction of chlor- and iodnitrophenols or anisols, when he found that iodine was removed just as bromine was, but that chlorine was not replaced by hydrogen. On the other hand he found that bromine could not be removed from derivatives of ortho- or paranitrophenols, as was to be expected from the work of previous observers. From his experiments he infers that bromine or iodine is replaced by hydrogen under the influence of tin and hydrochloric acid, when it stands in the ortho position to the two negative groups (OH. Br. NO_2. 1, 2, 3), although he has not yet succeeded in bringing an absolute proof that this is the constitution of the substances with which he worked.

Our experiments proved that when tribromdinitrobenzol was treated with a mixture of tin, hydrochloric acid, and a little alcohol,†† all three of the atoms of bromine were replaced by hydrogen, the product being metaphenylene diamine. Schlieper's inference given in the preceding paragraph, therefore, is not of general application, as, if this were the case, only one atom of bromine would have been removed from the tribromdinitrobenzol, since only one of them is in the ortho position to both of the nitro groups, the constitution of this substance being Br. NO_2. Br. NO_2. Br. H. It is to be observed also that the conversion of unsymmetrical brommetadinitrobenzol into metaphenylene

* Baessmann, Ann. Chem. CXCI. 244.

† Jackson and Bancroft, these Proceedings, XXIV. 299.

‡ Jackson and Bentley, these Proceedings, XXVI. 95.

§ Schlieper Ber. d. ch. G., 1892, p. 552.

‖ Hübner Petermann, Ann. Chem. CXLIX. 135.

¶ Ann. Chem. CCIX. 360.

** Ber. d. ch. G., XXVI. 2465.

†† Schlieper used stannous chloride and hydrochloric acid in his work, and it is possible that this difference may have modified the result.

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diamine, observed by Zincke and Sintenis, is not in harmony with this inference of Schlieper. Although, therefore, the diortho position is not essential to the removal of bromine by tin and hydrochloric acid, there is no doubt that Schlieper is right in considering it the most favorable position for this purpose, as the replacement by hydrogen of an atom of bromine standing between two nitro groups has been repeatedly observed in this laboratory with comparatively weak reducing agents, such as sodium malonic ester, and probably sodium acetacetic ester, or sodic ethylate.

In trying to find the cause of the replacement of all three atoms of bromine by hydrogen in the reduction of tribromdinitrobenzol the most obvious theory was that the attachment of the atoms of bromine to the benzol ring was weakened by the presence of the two negative nitro groups, as is so frequently observed in other reactions. If this was the case, the bromine would be removed before the nitro groups were reduced, and tribromphenylene diamine would not lose its bromine on treatment with tin and hydrochloric acid. Upon trying this experiment, however, we found that the whole of the bromine was removed from the tribromdiamine as easily as from tribromdinitrobenzol.* It follows, therefore, that the nitro groups are not the cause of the easy removal of the three atoms of bromine in the reduction of tribromdinitrobenzol. A parallel experiment with dibromphenylene diamine showed that this substance gave up its bromine with much more difficulty than the corresponding tribrom compound, for whereas the tribrom derivative was converted into phenylene diamine in a few minutes, it took over twelve hours to bring about the same change in the dibrom compound. It is evident from these unexpected results that the removal of the bromine atoms depends in part upon their position toward each other, and this is not strange, as in other cases it has been observed that three bromine atoms, when in the symmetrical position on a benzol ring, are more loosely attached than two in the meta position; but this is not the only cause of their removal, since symmetrical tribrombenzol is not reduced by tin and hydrochloric acid. It would seem, therefore, that the replacement of these atoms of bromine is caused principally by the fact that there are other radicals attached to the ring, with little regard to the nature of these radicals, as the highly positive amido groups apparently produce the same effect as the highly negative nitro radicals. An additional argument for this conclusion

* Other reagents, for instance sodic ethylate or sodic hydrate, do not remove bromine from the diamine.

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was furnished by experiments on the reduction of tribromaniline which was converted into dibromaniline by the action of tin and hydrochloric acid for a few hours. From the facts at present known we are unable to deduce any rule in regard to the position which these other radicals must occupy in order to cause the replacement of bromine by hydrogen, when the compound is treated with tin and hydrochloric acid.

After we had found, as just described, that the bromine was removed by the action of tin and hydrochloric acid upon tribromdinitrobenzol, we turned our attention to the study of the bromine derivatives of metaphenylene diamine, as only one of these had been described, — a dibromphenylene diamine, which Hollemann * stated he had obtained by the action of bromine water on the chloride of phenylene diamine. He gives, however, neither melting point nor analysis of his substance. Upon trying to repeat his preparation we found that bromine water converted the chloride of phenylene diamine (or the free base suspended in water) into a tribromphenylene diamine melting at 158°. As the product is the same, when an insufficient quantity of bromine is used, a portion of the phenylene diamine remaining unaltered in this case, the statement of Hollemann must have rested on an error of observation. A paper by Vaubel,† which appeared after our work on this subject was finished, confirms our result, as he found by a volumetric method that three atoms of bromine are substituted for hydrogen in the molecule of phenylene diamine, when it is treated with a mixture of potassic bromide, sulphuric acid, and potassic bromate. We have made the same tribromphenylene diamine by the action of zinc dust and acetic acid on the tribromdinitrobenzol; this method of preparation proves that its constitution is Br. NH_2. Br. NH_2. Br. H.

A dibromphenylene diamine can be obtained by the action of bromine in excess upon phenylene diacetamide. The dibromphenylene diacetamide melts at 259° to 260°; the free base at 135°. We have not succeeded in determining the constitution of this dibromphenylene diamine. Nor have we obtained the corresponding monobromphenylene diamine. A monobromphenylene diamine belonging to another series was obtained, however, by reducing tetrabromdinitrobenzol melting point 227° with tin and hydrochloric acid; it melts at 93°–94°, and from our experiments on the reduction of tribromdinitrobenzol there can be little doubt that it has the symmetrical constitution Br. H. NH_2. H. NH_2. H. When treated with bromine three atoms are sub-

* Zeitschr. f. Chem. 1865, p. 555.

† Journ. Prakt. Chem. [2] XLVIII. 75.

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stituted for three of hydrogen in its molecule, and the tetrabromphenylene diamine is formed, which melts at 212°–213°.

The presence of the bromine in the molecule of metaphenylene diamine has a strong effect on its tendency to form salts and on the composition of the salts formed. The tetrabrom and tribrom compounds do not form salts under ordinary conditions, but tribromphenylene diamine can be converted into its chloride by passing hydrochloric acid through a solution of it in benzol; this salt, however, gives up part of its hydrochloric acid at ordinary temperatures, the whole of it at 100°. The dibromphenylene diamine, on the other hand, forms salts more easily, and its chloride is only partially decomposed at 100°, while the bromide of this base seems to be even more stable. All three of these salts contain but one molecule of the acid, the chloride of dibromphenylene diamine, for example, having the following formula $C_6H_2Br_2NH_3ClNH_2$. The monobromphenylene diamine forms salts still more easily, and they are also more stable. The bromide contains two molecules of hydrobromic acid having the formula $C_6H_3Br(NH_3Br)_2$. We have also prepared the tribromphenylene diacetamide, which does not melt at 330°, and the tribromphenylene diurethane melting at 212.°

Experimental Part.

Tribrommetaphenylene Diamine $C_6HBr_3(NH_2)_2$.

The most convenient method for preparing this substance consists in passing a stream of air and bromine vapor into a solution containing metaphenylene diamine, for instance that obtained by adding sodic hydrate or carbonate to the product of the reduction of metadinitrobenzol with tin and hydrochloric acid until all the tin is precipitated and filtering out the hydrate of tin. In adding the bromine an excess must be avoided, as this turns the product black, and we have therefore found it well to filter the precipitate out by means of cheese-cloth as fast as a sufficient quantity of it was formed, continuing the action of the bromine vapor on the successive filtrates as long as a precipitate appeared. The crude product, which was always dark colored, was dried, and then crystallized from alcohol containing a little benzol until it showed the constant melting point 158°, when it was dried at 100° and analyzed with the following results: —

I. 0.1459 gram of the substance gave by the method of Carius 0.2392 gram of argentic bromide.

II. 0.2022 gram of the substance gave 14.65c.c. of nitrogen at a temperature of 19° and a pressure of 771.9 mm.

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	Calculated for $C_6HBr_3(NH_2)_2$.	Found. I.	II.
Bromine	69.56	69.78	
Nitrogen	8.11		8.21

These analyses prove that the substance is tribromphenylene diamine, and therefore our experimental result does not agree with that of Hollemann,* who stated that he obtained a dibromphenylene diamine by the action of bromine water on a solution of the chloride of phenylene diamine. As it was possible that this difference in the results of the action might be due to the fact that Hollemann used a salt of phenylene diamine, whereas we used in our first experiments the free base dissolved and suspended in water, we repeated our experiment with a solution of the chloride of phenylene diamine, and obtained precisely the same result as with the free base, that is, the tribromphenylene diamine melting at 158°. We are therefore forced to the conclusion that Hollemann's statement is due to an error in observation.

Properties. Tribromphenylene diamine crystallized from alcohol appears in long slender needles united longitudinally into ribbons with the ends serrated so strongly that they look like combs. It is white, with marked silky lustre, and melts at 158°. It is not very soluble in cold but freely in hot alcohol; somewhat more soluble in methyl than ethyl alcohol; freely soluble in acetone; soluble in ether, benzol, chloroform, glacial acetic acid, or carbonic disulphide; very slightly soluble in ligroine, but good crystals may be obtained from its solution in hot ligroine; essentially insoluble in water. Strong hydrochloric acid dissolves it easily in the cold, depositing after long standing white transparent crystals which soon turn brown; on heating the solution in hydrochloric acid it turned dark brown, almost black, showing decomposition of the substance; the formation of a similar nearly black decomposition product was brought about at once by cold strong nitric acid. Cold strong sulphuric acid dissolved the tribromphenylene diamine at once, the solution having a purplish tint, which turned to dark brown if it was allowed to stand for some time, or if it was stirred in a current of air for a short time. Nevertheless on one occasion a white solid was obtained, but before it could be collected a black spot appeared in one part of it which sped rapidly through the whole mass. Dilute sulphuric acid had no apparent effect on it in the cold, but decomposed it when hot. These observations show that the presence of the three atoms of bromine has destroyed in great measure the basic

* Zeitsch. für Chem. 1865, p. 555.

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properties of the phenylene diamine; but still it is possible to prepare salts of our substance, if proper precautions are observed, and the chloride is described somewhat later in this paper. Potassic hydrate, even when a boiling concentrated solution was used, produced no effect upon it.

When the tribromphenylene diamine is treated with tin and hydrochloric acid it is converted into phenylene diamine. The details of this work are given later in this paper. The success of this experiment suggested to us that the bromine might be removed also by other reagents; accordingly we heated some tribromphenylene diamine dissolved in benzol and alcohol with sodic ethylate, the action in one trial being continued for four days, but at the end of this time we recovered nearly the whole of the tribromphenylene diamine taken, and although the filtrate after treatment with nitric acid and argentic nitrate gave a slight precipitate, we ascribe this rather to the complete decomposition of a small portion of the substance (indicated by the dark brown color of the product) than to any simple reaction. As therefore sodic ethylate had no action, it did not seem to us worth while to try other experiments with less energetic reagents.

Chloride of Tribromphenylene Diamine $C_6HBr_3NH_3ClNH_2$. Although the tribromphenylene diamine forms no salts under ordinary conditions, we hoped that we might obtain its chloride by the method which yielded such excellent results to Gattermann* when he applied it to the tribromaniline. Accordingly hydrochloric acid gas was passed into a solution of tribromphenylene diamine in benzol, until it ceased to form a white precipitate, and the liquid fumed strongly. The precipitate was then filtered out, and dried by pressing between filter paper as quickly as possible, after which it was analyzed as follows: — 0.3096 gram of the salt lost 0.0272 gram of hydrochloric acid at 100°.

	Calculated for $C_6HBr_3NH_3ClNH_2$.	Found.
Hydrochloric Acid	9.56	8.79

The residue was entirely free from hydrochloric acid. This result is not so near the theoretical percentage as could be wished, but nevertheless proves that the salt is a monochloride of tribromphenylene diamine. The poor result is undoubtedly to be ascribed to the instability of the compound, which lost as much as 3.3 per cent of its weight from standing four days in a desiccator over sulphuric acid, and therefore might well have lost the 0.77 of one per cent during the drying on

* Ber. d. ch. G., XVI. 636.

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filter paper. The chloride as obtained was of a light brown color, although it is probably white when perfectly pure, and as indicated by the description of its analysis is very unstable, decomposing slowly in dry air at ordinary temperatures, quickly and completely when heated to 100°. We should judge that it was somewhat more stable than the chloride of tribromaniline prepared by Gattermann,* as might be expected from the presence of the second amido group. It seems to be soluble in strong hydrochloric acid since the tribromphenylene diamine dissolves in this reagent, but it is decomposed by water.

Tribromphenylene Diacetamide, $C_6HBr_3(NHC_2H_3O)_2$. This substance was made by treating tribromphenylene diamine with acetyl chloride, using anhydrous benzol as a solvent. The action began even in the cold as shown by the deposition of a white precipitate, but to make certain that it was complete the mixture was heated under a return-condenser for one hour. At the end of this time the white sandy precipitate was filtered out, and purified by extraction with glacial acetic acid, followed by recrystallization from the same solvent boiling. It was dried at 100°, and analyzed with the following results: —

I. 0.2726 gram of the substance gave 0.3561 gram of argentic bromide by the method of Carius.

II. 0.2548 gram of substance gave 0.3358 gram of argentic bromide.

	Calculated for $C_6HBr_3(NHC_2H_3O)_2$.	Found. I.	II.
Bromine	55.94	55.59	56.08

Properties. The tribromphenylene diacetamide crytallizes from hot glacial acetic acid in bunches of small white plates much longer than they are broad, which have square ends and frequently radiate from a centre; from alcohol in radiating groups of compound crystals made up of needles united longitudinally. It does not melt at 330°, and is very slightly soluble in all the common solvents. The best solvent for it is hot glacial acetic acid, but it is far from freely soluble even in this.

Tribromphenylene Diurethane, $C_6HBr_3(NHCOOC_2H_5)_2$. Five grams of tribromphenylene diamine were boiled with about twice the amount of chlorocarbonic ester required by the theory in a flask with a return condenser for three hours. The crude product (which weighed 6.5 grams), was purified at first by precipitating the substance with ligroine from its solution in a mixture of benzol and alcohol, afterward by

* Ber. d. ch. G., XVI. 636.

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recrystallization from a mixture of alcohol and ligroine, or alcohol and water, until it showed the constant melting point 212,° when it was analyzed with the following results: —

I. 0.3036 gram of the substance gave by the method of Carius 0.3454 gram of argentic bromide.

II. 0.1945 gram of the substance gave 0.2239 gram of argentic bromide.

	Calculated for $C_6HBr_3(NHCOOC_2H_5)_2$.	Found. I.	II.
Bromine	49.08	48.42	48.99

Properties. The tribromphenylene diurethane when deposited from alcohol forms very small crystalline masses, which under the microscope are seen to be rosettes made up of what at first sight appear to be short needles, but on closer examination prove to be groups of finer needles united longitudinally, since they betray their complex nature by the frayed or brushlike appearance of their ends, which resemble a partially untwisted cord. Its color is white, and it melts at 212°. It is soluble in cold alcohol, easily soluble in hot; easily soluble in chloroform, or acetone, less so in ether; somewhat soluble in cold benzol, easily soluble in hot, from which it crystallizes in the same form as from alcohol, but not so well; slightly soluble in carbonic disulphide even when hot; essentially insoluble in ligroine. Water dissolves it to a very slight extent when hot. Hydrochloric acid produced no apparent effect hot or cold; sulphuric acid did not act on it in the cold, but when hot dissolved it; from this solution it seemed to be precipitated unchanged by water, if the heating had not been long continued, but long heating with the strong acid decomposed it. A concentrated solution of potassic hydrate seemed to have no effect on it in the cold, but when heated turned the substance brown, and finally black with apparently complete decomposition. The best solvent for it is alcohol diluted with either water or ligroine.

Reduction of Tribromdinitrobenzol.

Tribromdinitrobenzol (melting at 192°, made from symmetrical tribrombenzol) was reduced by treatment either with zinc and acetic acid, or with tin and hydrochloric acid, but the products were different in the two cases as described in the following sections.

Reduction with Zinc Dust and Acetic Acid. This reduction we found it best to carry on in an atmosphere of carbonic dioxide, as the liquid showed a strong tendency to turn black during the process.

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The zinc dust contained in a flask kept full of carbonic dioxide was covered with acetic acid of 80 per cent, and the tribromdinitrobenzol added in small quantities at a time. If the zinc dust and tribromdinitrobenzol were mixed together before adding the acetic acid the action was far too violent; in fact, once the mixture took fire when the acetic acid was added. Even when the process was carried on as directed, the action was energetic at first, but later it was necessary to warm the flask gently to assist the reaction. The products were in part dissolved in the aqueous liquid, which with all our precautions was invariably dark colored, and partly appeared as a crystalline powder in the bottom of the flask. The insoluble part was recrystallized from benzol, by which it was separated into a large fraction melting at 158°, a small amount of substances melting at a lower temperature, and a little unaltered tribromdinitrobenzol. The principal product was shown to be tribromphenylene diamine by its melting point, but to confirm this it was dried at 100° and analyzed, when it gave the following results: —

0.2337 gram of the substance gave by the method of Carius 0.3786 gram of argentic bromide.

	Calculated for $C_6HBr_3(NH_2)_2$.	Found.
Bromine	69.56	68.95

This percentage of bromine, although not agreeing with that calculated so closely as could be wished, is yet accurate enough when taken in connection with the melting point to leave no doubt as to the nature of the substance formed, and therefore we did not attempt to get a number nearer to the theoretical.

The amount of tribromphenylene diamine formed by the reduction was considerable; in one case 10 grams of tribromdinitrobenzol yielded 4.7 grams of it, and 0.9 gram of tribromdinitrobenzol were recovered unaltered, so that the percentage of the theoretical yield was 60.6. The remainder of the product was contained in the aqueous solution (and to a less extent in the small amount of lower melting material from the benzol mother liquors); it undoubtedly consisted of phenylene diamine, from which part or all the bromine had been removed, since the aqueous solution gave tribromphenylene diamine when treated with bromine water, a behavior which, as we have already stated, belongs to solutions of phenylene diamine and its salts.

Reduction with Tin and Hydrochloric Acid. We found it best to proceed as follows: Some granulated tin with a piece of platinum and about 300 c.c. of strong hydrochloric acid were gently warmed in a

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flask closed by a cork provided with a Bunsen valve, until the greater part of the air had been expelled. 10 grams of tribromdinitrobenzol mixed with enough alcohol to make a thick paste were then added, and the reduction was allowed to go on, warming or cooling the mixture as was necessary, until all the organic substance had dissolved. If the solution thus obtained was a strong one, beautiful white needles of a double tin salt were deposited on cooling; if it was more dilute, they usually appeared after standing a day, but in some cases the substance obstinately refused to crystallize. The crystals were filtered out, and decomposed in concentrated solution with sulphuretted hydrogen, when the filtrate from the sulphide of tin left on evaporation a crystalline solid which after three crystallizations from a mixture of water and hydrochloric acid was analyzed with the following results.

I. 0.2220 gram of the substance gave 31.8 c.c. of nitrogen at a temperature of 26.5° and a pressure of 756.9 mm.

II. 0.2983 gram of the substance gave by the method of Carius 0.4727 gram of argentic chloride.

	Calculated for $C_6H_4(NH_3Cl)_2$.	Found. I.	II.
Nitrogen	15.47	15.79	
Chlorine	39.21		39.17

The tin and hydrochloric acid had therefore reduced both the nitro groups, and also removed all three of the atoms of bromine from the tribromdinitrobenzol; and that the removal of bromine had taken place from the whole of the substance was made probable by the fact that all the organic matter dissolved, whereas the tribromphenylene diamine, as already stated in this paper, is insoluble in water or dilute hydrochloric acid. An additional confirmation of the presence of phenylene diamine was given by the following experiment. The base set free from the soluble chloride analyzed above was treated with bromine water, when a precipitate was formed, which after recrystallization from alcohol containing a little benzol melted at 158°, and was therefore the tribromphenylene diamine which is made in this way from metaphenylene diamine.

When we began work on this subject we made many analyses of the double tin salt which crystallized out of the solution after the reduction; but although in two different preparations we obtained numbers agreeing with the salt $C_6H_4(NH_3ClSnCl_2)_2$ discovered by Gudemann,* we found that in others its composition varied so much that no certain

* Zeitsch. für Chem. 1865, p. 51.

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inference in regard to the composition of the base formed could be drawn from these analyses, and therefore prepared the salt free from tin as described above.

After we had shown by the work just described that the three atoms of bromine are removed from tribromdinitrobenzol by tin and hydrochloric acid, it became of interest to determine whether their removal was due to the effect of the two nitro groups upon them. This seemed a probable supposition, because it has been repeatedly observed that atoms of bromine can be easily removed from the benzol ring when they stand in the ortho position to nitro groups, and work done in this laboratory has proved that this tribromdinitrobenzol is a very reactive body, but on the other hand it did not seem likely that the bromine atoms would be removed before the reduction of the nitro groups, as all previous experience seems to show that the latter are much more easily attacked than the former. It was obvious that this point could be decided by trying the action of tin and hydrochloric acid on tribromphenylene diamine, for none of the bromine would be removed from this substance if this action depended on the presence of the nitro groups. Accordingly five grams of tribromphenylene diamine were mixed with tin and hydrochloric acid and a piece of platinum added to increase the action. In the cold no change was observed, and therefore the mixture was warmed on the water bath, when, after a vigorous reaction had gone on for a short time, all the organic matter dissolved. The brown clear solution deposited crystals as it cooled, but disregarding these the whole was treated with an excess of sodic hydrate and extracted with ether repeatedly. The residue from the ethereal extracts was an oil, which solidified after it had been scratched with a sharp glass rod, and then melted at about 62°. There was little doubt therefore that the substance was metaphenylene diamine, which melts at 63°, and this view was confirmed by the following observations. The substance gave a white salt with hydrochloric acid soluble in water, but nearly insoluble in hydrochloric acid. To a solution of this chloride bromine water was added, taking care to avoid an excess; this produced a white precipitate, which after recrystallization from benzol melted at 158°, and was therefore tribromphenylene diamine. It follows from this experiment (which was repeated several times) that tribromphenylene diamine gives up all its bromine to tin and hydrochloric acid, and therefore that the removal of the bromine atoms does not depend on the loosening effect of the two nitro groups.

Action of Tin and Hydrochloric Acid on Tribrombenzol and on Tribromaniline. After we had shown, as just described, that all the bro-

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mine can be removed from tribrommetaphenylene diamine by the action of tin and hydrochloric acid, it occurred to us that the comparatively loose attachment of the bromine to the benzol ring might be due to the fact that the three atoms of bromine were in the symmetrical position, since Blau has shown that one of these atoms in tribrombenzol can be replaced by the methoxy radical, and we have confirmed this observation. This hypothesis seemed the more probable because dibrommetaphenylene diamine is reduced under these conditions much more slowly than the tribrom compound. If this view is correct, tin and hydrochloric acid should remove bromine from the symmetrical tribrombenzol, and accordingly we tried the following experiment. Ten grams of tribrombenzol were mixed with granulated tin and strong hydrochloric acid, a piece of platinum added to promote the action, and enough alcohol to dissolve a large part of the tribrombenzol. The reason for adding the alcohol was that we thought the action of the reducing agent on the tribrommetaphenylene diamine might be in part due to its tendency to dissolve in the acid, or still more to the solubility of the products of the reduction in the acid, and we hoped by the addition of the alcohol to establish similar favorable conditions in the case of the tribrombenzol. The mixture was heated under a return condenser on the water bath for a week. At the end of this time enough water was added to precipitate any brombenzols which might be present, and the heavy crystalline precipitate thus obtained was filtered, and washed until it was free from stannous chloride. It was then dried and weighed, when 9.5 grams were obtained, so that the loss was no greater than would be expected from the rough way in which the experiment had been carried on. This substance melted at 120°, and was therefore unaltered tribrombenzol (melting-point 119.6°). It follows from this experiment that tin and hydrochloric acid do not remove bromine from symmetrical tribrombenzol, and, therefore, that the conversion of tribrommetaphenylene diamine into metaphenylene diamine by these reagents is not due to the symmetrical position of the bromine atoms, although it may have a subsidiary effect in assisting this conversion.

An experiment similar to that just described was tried with 10 grams of tribromaniline. The conditions were exactly the same as those used for tribrombenzol, given at length in the preceding paragraph. Upon adding water to precipitate the organic substances, after the reduction was completed, only a very small precipitate was formed, which in time changed to long needles. This precipitate weighed less than 0.5 gram, and as it melted at 118° was undoubtedly unaltered tribromaniline. The filtrate from this precipitate was treated with

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an excess of sodic hydrate, the precipitate thus formed dissolved in hydrochloric acid, and reprecipitated with sodic hydrate in excess to remove the hydrates of tin as completely as possible, and then extracted with alcohol. The alcoholic extract deposited long white needles, which melted at 78°–79°, and were therefore probably dibromaniline. To establish the nature of the substance more fully, we tried the following experiments. The amido group was replaced by bromine, when a product was obtained melting at 44°, the melting point of the unsymmetrical tribrombenzol, and this when treated with nitric acid was converted into the mononitrotribrombenzol melting at 93°. There can be no doubt therefore that the tin and hydrochloric acid have removed one of the atoms of bromine from the ortho position to the amido group, replacing it by hydrogen. A quantitative experiment gave the following results, — 10 grams of symmetrical tribromaniline yielded after reduction for six hours 5 grams of dibromaniline. from which were obtained 5 grams of unsymmetrical tribrombenzol, and from this 5.2 grams of tribromnitrobenzol.

Dibrommetaphenylene Dicetamide, $C_6H_2Br_2(NHC_2H_3O)_2$.

Whereas free metaphenylene diamine gives a tribrom derivative, when treated with bromine water, we have obtained only the dibrom compound from metaphenylene diacetamide, even when a considerable excess of bromine was used. The samples analyzed were prepared by the method given below, but a better method discovered later is described after the analyses, — Metaphenylene diacetamide was dissolved in common acetic acid with the aid of gentle heat, and treated at first with bromine, and afterward with bromine water, until a slight excess had been added. The new substance separated from the solution as it was formed, and after standing a short time it was filtered out, and purified by crystallization from hot glacial acetic acid until it showed the constant melting point 259°, when it was dried at 100°, and analyzed with the following results : —

I. 0.2471 gram of the substance gave 19 c.c. of nitrogen at a temperature of 29° and a pressure of 754.3 mm.

II. 0.2145 gram of the substance gave by the method of Carius 0.2294 gram of argentic bromide.

III. 0.2033 gram of the substance gave by the method of Carius 0.2198 gram of argentic bromide.

	Calculated for $C_6H_2Br_2(NHC_2H_3O)_2$.	Found. I.	II.	III.
Nitrogen	8.00	8.33		
Bromine	45.71		45.52	46.01

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The substance can be obtained more expeditiously in a pure state by avoiding the preparation of solid phenylene diacetamide as follows. A strong ethereal solution of phenylene diamine is treated with acetic anhydride until a portion gives a white or slightly yellow precipitate with bromine (if unaltered phenylene diamine is present, the precipitate will be brown). When this is the case, an excess of bromine water is added to the solution, and the mixture stirred vigorously until the precipitation is complete. The product is essentially pure without recrystallization.

Properties. The dibrommetaphenylene diacetamide crystallizes by slow evaporation from an alcoholic solution in very small, rather short prisms. If on the other hand the crystallization takes place by cooling, obscurely crystalline masses are obtained in which it is hard to make out any definite form; they seem to be prisms coated with needles. Its color is white, and it melts at 259° to 260° with decomposition, as is shown by the fact that the melted mass turns black and puffs up to many times its original volume. On account of this decomposition it is necessary to keep the melting tube in the oil bath as little as possible in determining the melting point. If the substance is allowed to remain in the bath while its temperature is raised, a melting point as low as 250° may be obtained. It is very slightly soluble in cold alcohol, and only a little more soluble in hot; very slightly soluble in benzol, chloroform, or carbonic disulphide; somewhat more soluble in acetone, or glacial acetic acid; essentially insoluble in ether or ligroine. The best solvent for it is glacial acetic acid or alcohol, although it is soluble in the latter only sparingly and with great difficulty. It is very slightly soluble in boiling water, insoluble in cold. Strong hydrochloric acid saponifies it quickly when the two are gently heated together; strong sulphuric acid dissolves it in the cold, but without decomposition, as the unaltered substance is obtained by diluting and neutralizing the acid, it decomposes the substance when hot; if dilute it has no apparent effect when cold, but when heated saponifies and afterward decomposes it; strong nitric acid dissolves it quickly when cold, but the substance is recovered unaltered on neutralization; when hot it decomposes it. A strong solution of potassic hydrate saponifies it when hot.

Dibrommetaphenylene diamine, $C_6H_2Br_2(NH_2)_2$. — This substance was obtained by removing the acetyl groups from the preceding compound as follows: 10 grams of the dibromphenylene diacetamide were heated with from 30 to 40 c.c. of commercial strong hydrochloric acid for half an hour in a flask with a return-condenser; at the end of this

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time the solid was completely dissolved, and the liquid had taken on a dark brownish red color. After it was cool, the solution was treated at first with sodic carbonate, and finally with sodic hydrate in excess, which precipitated a brown solid. This was filtered out, washed until free from alkali, and purified by crystallization from boiling water containing a little alcohol until it showed the constant melting point 135°. In this recrystallization long heating of the solution should be avoided, as this seems to decompose the substance with precipitation of a black compound. The pure substance was dried at 100° and analysed with the following result: —

0.3872 gram of the substance gave by the method of Carius 0.5473 gram of argentic bromide.

	Calculated for $C_6H_2Br_2(NH_2)_2$	Found.
Bromine	60.15	60.16

Properties. — The dibromphenylene diamine crystallizes in fine needles which are white, if the substance is perfectly pure, but usually show a brownish color, which is due to an impurity so slight that it has no effect upon the analysis. It melts at 135°, and is easily soluble in alcohol whether hot or cold. It is very soluble in acetone; easily soluble in ether, somewhat less soluble in benzol, or chloroform, if cold. easily soluble, if hot; slightly soluble in cold carbonic disulphide, soluble when hot; very slightly soluble in cold ligroine, more soluble when it is hot; nearly insoluble in cold water, slightly soluble in hot, but it is decomposed, if boiled for some time with water. The best solvent for it is dilute alcohol. It shows a much stronger tendency to form salts than the tribromdiamine, as it dissolves in either hydrochloric acid or hydrobromic acid, and the solution leaves the salt on spontaneous evaporation; cold strong sulphuric acid turns it purple, and then dissolves it, but upon standing the sulphate separates from this solution in glistening white or pinkish plates, which seem to belong to the monoclinic system; when hot, sulphuric acid decomposes it; strong nitric acid dissolves it, and then decomposes it even in the cold forming a brown solution. A cold solution of potassic hydrate has no effect upon it, but, if the mixture is heated, decomposition sets in as shown by the appearance of a black color. We selected for further study the chloride and the bromide of the base with the results described below.

We have also studied the action of tin and hydrochloric acid on the dibromphenylene diamine. For this purpose 3.75 gram of the dibromphenylene diamine were warmed with tin, hydrochloric acid, and pla-

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tinum under the conditions already described when speaking of the tribromphenylene diamine. The action in this case was very slow; whereas the tribrom compound dissolved after treatment for a short time, it was necessary to carry on the action for over twelve hours in order to bring the dibromamine into solution. The product yielded an oily free base, smelling like metaphenylene diamine, which, however, we did not succeed in obtaining in a solid state. It gave an easily soluble chloride, so there can be no doubt that bromine was removed. We are unable to determine with certainty the cause of the very slow removal of the bromine from the dibromphenylene diamine; it is possible that it is only mechanical, as it was observed that this substance showed a tendency to form a coating on the surface of the tin, or on the other hand it may be that the symmetrical position of the three atoms of bromine in the tribromphenylene diamine has the effect of loosening their attraction for the benzol ring. This latter explanation seems to us the more probable.

Chloride of Dibromphenylene Diamine, $C_6H_2Br_2NH_3ClNH_2$. This salt can be made by dissolving the diamine in strong aqueous hydrochloric acid and allowing the solution to evaporate spontaneously, but we did not use this method in preparing the salt for analysis, because we feared that it might undergo a partial decomposition, if deposited from a solution containing water. We therefore prepared it by passing hydrochloric acid gas through a solution of the diamine in benzol, until the liquid fumed strongly, and no more solid matter was deposited. The precipitate thus obtained was pressed repeatedly between filter paper, and dried for one hour over sulphuric acid, when it gave the following result on analysis: —

0.2173 gram of the salt gave by the method of Carius 0.3713 gram of the mixture of argentic chloride and bromide.

	Calculated for $C_6H_2Br_2NH_3ClNH_2$	Found.
Chlorine and Bromine	64.63	64.28

The chloride of dibromphenylene diamine is much more stable than the corresponding tribrom-compound, since, whereas the chloride of tribromphenylene diamine lost all its hydrochloric acid when heated to 100° for a short time, the chloride of dibromphenylene diamine showed a loss under the same conditions of only 5 per cent instead of the 12.07 per cent, which represents the loss, if the whole of its hydrochloric acid had been given up. Further the salt of the dibrom compound can be made by the action of a strong aqueous solution of

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hydrochloric acid upon the free base, while, although the tribrom base dissolves in strong hydrochloric acid, we have not succeeded in obtaining the solid chloride from this solution. It must not be inferred from this comparison, however, that the chloride of dibromphenylene diamine is especially stable, for this is not the case, since it loses nearly 4 per cent of its weight by standing in a desiccator, and is also decomposed by water.

Bromide of Dibromphenylene Diamine, $C_6H_2Br_2NH_3BrNH_2$. — This substance was made by adding dibromphenylene diamine to distilled hydrobromic acid (boiling point 123°) until it ceased to dissolve easily in the cold. A good deal of trouble was encountered in obtaining the solid salt from this solution, as heating decomposed it, and none of the organic solvents miscible with water gave a precipitate with it; spontaneous evaporation indeed gave the salt, but as we did not know its properties at the time of the preparation we were afraid of decomposition during such long standing, and accordingly proceeded as follows: The aqueous solution was covered with a rather thick layer of ether, and the whole stirred vigorously for about a quarter of an hour; under this treatment the bromide crystallized out in the lower part of the ether, when it was separated, washed with ether, and dried in a desiccator over sulphuric acid. It then gave the following results on analysis: —

I. 0.4433 gram of the substance gave by the method of Carius 0.7191 gram of argentic bromide.

II. 0.3014 gram of the substance gave 0.4884 gram of argentic bromide.

	Calculated for $C_6H_2Br_2NH_3BrNH_2$	Found. I.	II.
Bromine	69.16	69.04	68.96

The sample used in the first analysis had been dried for only three hours, that for the second had stood in a desiccator over sulphuric acid for three days, showing that the salt is stable under these circumstances. The bromide is therefore more stable than the chloride, as that lost nearly four per cent of its weight in a desiccator, which amounts to one third of the acid that it contains.

The bromide of dibromphenylene diamine forms white needles, which turn brown quickly, when exposed to the air. It is decomposed by water, but is soluble in ethyl, or methyl alcohol, the solution apparently decomposing on standing; insoluble in ether, benzol, or ligroine.

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Reduction of Tetrabromdinitrobenzol. The tetrabromdinitrobenzol was prepared essentially by the method given by Bancroft and one of us,* but a few improvements in the process should be mentioned here. By using a large amount of glacial acetic acid the yield of tetrabrombenzol was materially raised. The details of this process will be found in our paper, "On the Behavior of Certain Halogen Derivatives of Benzol." In converting the tetrabrombenzol into the dinitro compound we found that the quantities of sulphuric acid and nitric acid used could be reduced to 50 c.c. of each for 10 grams of tetrabrombenzol, if the tetrabrombenzol was pure; if this was not the case the best method was to treat the tetrabrombenzol with the acid mixture, which had already been used once with tetrabrombenzol; the product of this action of the residual acid was then treated with one half the amount of fresh sulphuric acid and nitric acid needed for the complete conversion of the tetrabrombenzol into the dinitro compound, and in this way a nearly pure product was obtained at little expense of fuming nitric acid. With pure tetrabrombenzol the yield was very nearly quantitative, 100 grams giving 121 grams of a product melting at 220°, which after one recrystallization melted at 227°, the correct melting point for tetrabromdinitrobenzol; as 100 grams should give 122.8 grams, this makes the yield of this crude product over 99 per cent.

To reduce the tetrabromdinitrobenzol it was mixed with alcohol, tin, and hydrochloric acid, and the mixture heated on the water bath in a flask with a return condenser, more hydrochloric acid being added from time to time. When the volume of liquid became unpleasantly large, it was evaporated in an open dish to a convenient volume, and returned to the flask with fresh alcohol and acid. After the organic matter had gone completely into solution, which usually happened after boiling for about 70 hours, the liquid was again concentrated and rendered strongly alkaline with crude sodic hydrate. The hydrate of tin was filtered out with cheese cloth, and dried as thoroughly as possible by sucking air through it, after which it was shaken repeatedly with rather large amounts of alcohol. The alcoholic extract thus obtained was freed from alcohol by distillation, followed by evaporation on the water bath, when an oil and an aqueous solution were left, which were separated, if possible, mechanically; if not, by shaking with ether. The oil obtained directly or from the ether solidified after a short time. The aqueous filtrate from the hydrate of tin with the liquid

* These Proceedings, XXIV. 289.

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separated from the oil was shaken with ether repeatedly, and the oil thus obtained added to the main portion. The aqueous solution after shaking with ether gave a very slight precipitate on the addition of bromine, but the amount of tetrabromphenylene diamine obtained in this way was so small that this treatment is hardly worth while. The principal product, after it had solidified, was purified by dissolving is in rather dilute alcohol and saturating the solution with suphuretted hydrogen, when it was warmed gently, and allowed to stand in a corked flask for some time; after filtering off the sulphide of tin it was evaporated to dryness, and the residue recrystallized from pure ligroine (boiling from 60°–70°) until it showed the constant melting point 93°–94°, when it was dried in a desiccator and analyzed with the following result: —

0.2117 gram of the base gave by the method of Carius 0.2113 gram of argentic bromide.

	Calculated for $C_6H_3Br(NH_2)_2$.	Found.
Bromine	42.79	42.48

Properties of Monobrommetaphenylene Diamine. It crystallizes from a mixture of benzol and ligroine in white spindle-shaped forms often a centimeter long; from benzol alone in bundles of small needles united longitudinally; from alcohol in not very well developed prisms apparently belonging to the monoclinic system and often twinned. It melts at 93°–94°, and is readily soluble in acetone, alcohol, ether, or chloroform; in benzol, or carbonic disulphide it is slightly soluble in the cold, more freely when hot; nearly insoluble in cold ligroine, difficultly soluble in hot; it is moderately soluble in cold water, as shown by the fact that such a solution gives a good precipitate with bromine water; in hot water it is even more soluble, the solution as it cools depositing oil drops, which later change to needles. The best solvent for it is a mixture of benzol and ligroine, but crystallization from pure ligroine is necessary to get a perfectly white product. It shows a tendency to separate from its solutions at first as an oil, and also to become decomposed, when in solution, forming a brown product.

The monobromphenylene diamine shows marked basic properties. Hydrochloric acid or hydrobromic acid gives with it a salt soluble in water, a description and analysis of the bromide formed in this way is given below; moderately strong sulphuric acid also gives a soluble salt, which forms white crystals when the solution is allowed to evaporate spontaneously; dilute nitric acid seems to have little action on it in the cold, but when hot converted it into a brown substance. Sodic hydrate

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seemed to have no action even when warmed with it for several minutes on the water bath. The constitution of this monobromphenylene diamine is probably NH_2. H. NH_2. H. Br. H, as the tribromdinitrobenzol made from symmetrical tribrombenzol loses all its bromine when reduced under the conditions used in obtaining the monobromphenylene diamine from tetrabromdinitrobenzol.

Bromide of Monobromphenylene Diamine, $C_6H_3Br(NH_3Br)_2$.

Monobromphenylene diamine was mixed with distilled hydrobromic acid (boiling point 124°–125°), and the liquid heated to boiling. The solid was then brought into solution by the careful addition of just the proper amount of water to the boiling solution, after which more of the hydrobromic acid was added, until crystallization began, when the mixture was allowed to cool; the crystals thus obtained were washed with hydrobromic acid and then with ether, dried by pressure with filter paper, and washed with ether a second time. After drying over sulphuric acid the salt was analyzed with the following result: —

0.2474 gram of the substance gave according to the method of Carius 0.3945 gram of argentic bromide.

	Calculated for $C_6H_3Br(NH_3Br)_2$.	Found.
Bromine	68.77	67.86

This analysis leaves much to be desired, but the result is near enough to show that the formula given above is correct. The salt forms colorless transparent glassy crystals, which look like cubes under the microscope; freely soluble in water, slightly in hydrobromic acid.

Tetrabromphenylene Diamine, $C_6Br_4(NH_2)_2$.

This substance was made by dissolving the monobromphenylene diamine, melting at 93°–94° in ether and adding a slight excess of bromine; the product, after recrystallization from a mixture of chloroform and ligroine, showed the constant melting point 212°–213°, when it was dried and analyzed with the following result: —

I. 0.2357 gram of the substance gave by the method of Carius 0.4166 gram of argentic bromide.

II. 0.2493 gram of the substance gave 0.4432 gram of argentic bromide.

	Calculated for $C_6Br_4(NH_2)_2$.	Found.	
		I.	II.
Bromine	75.47	75.22	75.67

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Properties of Tetrabromphenylene Diamine. It crystallizes in very small white needles, which melt at 212°–213°, and are freely soluble in benzol, chloroform, ether, acetone, or carbonic disulphide; slightly soluble in cold alcohol, freely in hot; almost insoluble in cold ligroine, slightly soluble in hot. The best solvent for it is a mixture of chloroform or benzol with ligroine. The tetrabromphenylene diamine has nearly, if not quite, lost the basic properties of a diamine, as was to be expected since it is loaded with so many negative bromine atoms. Hydrobromic acid had but little apparent action on it, even when hot, although the liquid deposited after long standing a few transparent crystals, which may have been the bromide.

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VIII.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

A REVISION OF THE ATOMIC WEIGHT OF ZINC.

FIRST PAPER: THE ANALYSIS OF ZINCIC BROMIDE.

By Theodore William Richards and Elliot Folger Rogers.

Presented April 10, 1895.

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Introduction.

In an account of a recent investigation on the occlusion of gases by the oxides of metals * it was shown that zincic oxide, in common with cupric and magnesic oxides, has the power of retaining important quantities of oxygen and nitrogen gases, even at very high temperatures. Hence it was evident that all determinations of the atomic weight of zinc depending upon the conversion of the metal into the oxide through the ignition of the nitrate must be influenced by a constant error, which has the tendency to make the results lower than the true value. In consideration of this fact, it becomes very important to review all of the results thus far obtained regarding the atomic weight of zinc, in order to determine how seriously the error in question may influence our accepted value. A chronological list † of the accessible data is given below.

* These Proceedings, XXVIII. 200, Richards and Rogers.

† Much assistance in preparing the list has been obtained from the works of Clarke, Meyer and Seubert, and others. The results have been recalculated with the assumption of the following atomic weights: O = 16, C = 12.002 Cl = 35.456, Ag = 107.93, H = 1.0075.

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1809.	Gay Lussac, Mém. d'Arceuil, II. 174	65.55
1811.	Berzelius, Pogg. Ann., VIII. 184	65.57
1842.	Jacquelain, An. de Chim. et de Phys. [3.], VII. 204 .	66.24
1844.	Favre, An. de Chim. et de Phys. [3.], X. 163 . . .	65.99
1844.	Erdmann, Berz. Jahresber., XXIV. 132, and Pogg. Ann., LXII. 612	65.05
1883.	Pelouze and Fremy, Chem., p. 55	65.07
1883.	Baubigny, Comptes Rendus, XCVII. 906	65.41
1883.	Marignac, Archiv. Sci. Phys. et Nat. [3.], X. 5, 193 .	65.30
1885.	Van der Plaats, Comptes Rendus, C. 55	?
1887.	Reynolds and Ramsay, J. Ch. Soc. Trans., LI. 854 .	65.67
1888.	Morse and Burton, Am. Chem. Journ., X. 311 . . .	65.27
1889.	Gladstone and Hibbert, J. Ch. Soc. Trans., LV. 443 .	65.44

The various results have been reached: —

1. By converting a known weight of metallic zinc into the oxide (Berzelius, Jacquelain, Erdmann, Morse and Burton).

2. By the evolution of hydrogen from acids by metallic zinc, the hydrogen being either measured or burned, (Jacquelain, Favre, Van der Plaats, Reynolds and Ramsay).

3. By the conversion of a salt of zinc into zincic oxide through ignition (Favre, zincic oxalate; Pelouze, zincic lactate; Baubigny, zincic sulphate).

4. By the determination of the electrolytic equivalent of zinc (Gladstone and Hibbert).

5. By analysis of a haloid salt of zinc (Marignac.)

The work of Morse and Burton by the first method is so far superior to the previous determinations made in the same way, that the the older ones may be wholly neglected. The two or three possibilities of infinitesimal error, such as the chance that the zinc might contain impurities taken from the glass used for its distillation, may be wholly neglected when compared with the great error due to the occlusion of nitrogen and oxygen. As the amount of this error is dependent upon the physical condition of the zincic oxide. it is impossible to make an accurate correction except by the actual determination of the gas in the oxide remaining from the determinations. From our own experiments* it would appear that a gram of zincic

* These Proceedings, XXVIII. 200.

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oxide obtained from the nitrate usually contains about 0.00057 gram of occluded gas; upon this basis Morse and Burton's result would become 65.458 instead of 65.269.

In considering the results obtained by the second method the results of Favre and Jacquelain may be rejected at once. Of Van der Plaat's results it is necessary to state only that some error must have crept in while recording his data, for it is inconceivable that 6.6725 grams of zinc should yield only 1.1424 litres of hydrogen. The work of Reynolds and Ramsay was much more careful and detailed; but the results varied very widely. Hydrogen evolved from very pure zinc was measured, with many precautions; but after the rejection of thirty-four experiments eleven more gave a value of 65.24, and still five more gave 65.47 as the atomic weight of zinc. Since the publication of their work many investigations have shown that the density of hydrogen is greater than the value assumed at that time. If a litre of the gas weighs 0.0901 * gram, and the atomic weight of hydrogen is taken as 1.0075 (O = 16.000) the atomic weight of zinc deduced from Reynolds and Ramsay's experiments becomes about 65.63.

The two older results obtained by the third method are worthy of no further mention. Baubigny's work upon the ignition of zincic sulphate is very interesting, but probably incomplete. It will be remembered that the value for copper obtained by the same method was too low, † owing, probably, to the occlusion of sulphuric acid by the cupric sulphate. It is not impossible that a similar error may have crept in here, for the conditions were similar; but it is probable that it is here counterbalanced by the retention of sulphur trioxide by the zincic oxide. In a series of experiments made in this laboratory pure zincic oxide obtained from the carbonate (see p. 163), was ignited to constant weight in an oxidizing atmosphere at a temperature above the fusing point of gold; ‡ it was then dissolved in dilute sulphuric acid which left no residue upon evaporation, and very gradually brought again to the same high temperature. In no case were we able to expel all of the sulphuric acid which we had added. Three experiments are appended: —

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* Lord Rayleigh and others.

† Richards, These Proceedings, XXVI. 275.

‡ Four grams of pure gold melted in fifteen minutes from the time of turning on the air blast in the furnace.

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Weight of Zincic Oxide before.	Weight of Zincic Oxide after.	Gain.
Grams.	Grams.	Grams.
1.03009	1.03032	0.00023
0.80243	0.80265	0.00022
1.03447	1.03473	0.00026
Average for 1 gram ZnO		0.00025

Gladstone and Hibbert deposited silver in one cell by means of a voltaic current, while zinc was being dissolved from an amalgamated plate in another. Although the experiments are interesting, it would appear from the results of Vanni * and others that the possibility of side reactions makes the strict applications of Faraday's law for the determination of atomic weights of rather doubtful efficacy. One would expect the method adopted to give a result larger than the true one.

Marignac's work upon the chloride of zinc and the double chloride of zinc and potassium is even less satisfactory than his investigations of other chlorine compounds; it merits no further notice.

It is evident from these statements that the three least unsatisfactory determinations are all vitiated to a greater or less extent by constant errors; the work of Morse and Burton by one which tends to lower the result; the work of Gladstone and Hibbert by one which may tend to raise the result; and the work of Baubigny by two which tend to counteract one another. One would expect the atomic weight of zinc to prove in the end equal to about 65.4.

It seemed very desirable to obtain a series of determinations which should be wholly different from any of these; and for this reason zincic bromide was chosen as the starting point of the present research. Additional advantages presented by the use of this substance are the fact of its ready and accurate analysis, and the fact that a determination of the ratio $2\,Ag : ZnBr_2$ would bring the element into a series of elements which have been determined by Stas and others with great precision in this way.

* Berichte d. d. Ch. G., XXIV., Ref. 882.

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Balances and Weights.

The preliminary determinations were made upon a long-armed Becker balance with the help of very carefully standardized platinized brass weights. The final determinations were made upon the admirable Troemer balance procured for the research upon copper, and subsequently used for those upon barium and strontium. The weights used in these final determinations were the same as those used in the researches just cited; they were compared with one another at the beginning and at the close of the research, with satisfactory results. All weighings were made by substitution, the tare weights being vessels as nearly as possible similar to those being weighed; and all were reduced to the vacuum standard by the usual formula.

The Specfic Gravity of Zincic Bromide.

In the course of recent investigations upon the atomic weights so many of the usually accepted specific gravities of hygroscopic substances have been found to be seriously in error, that it seemed advisable to redetermine the constant which influences the reduction to vacuum of the present results.

Pure zincic bromide was dried for a long time at a temperature of 200°, and then fused and heated for a short time at 300°. The pycnometer in which this drying was effected was then stoppered and cooled in a desiccator. Carefully dried toluol having a specific gravity of 0.8646 at 20°, when referred to water at 4°, was used as the liquid to be displaced. Toluol is convenient for the purpose, because so few inorganic substances are soluble in it, and because its volatility is not so great as to cause serious loss during the weighing, but is great enough to allow of the rapid drying of the exterior of the apparatus. The first sample of zincic bromide was made from very pure hydrobromic acid and ordinary pure zinc, and was distilled in an atmosphere of carbon dioxide; the second was made from the purest electrolytic zinc and the purest bromine. Both samples gave a perfectly clear dilute solution in water after the expulsion of the toluol on the steam bath after the experiment. The decanted toluol left upon evaporation on the steam bath only a trace of residue, which was insoluble in water. Water decanted from this residue gave no trace of precipitation with argentic nitrate; hence it is evident that zincic bromide is insoluble in toluol. The liquid contained in glass

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increases about 0.001 of its apparent volume for each degree of temperature; and the small appropriate correction is applied below.

SPECIFIC GRAVITY OF ZINCIC BROMIDE.

No. of Experiment.	Weight of $ZnBr_2$.	Temperature.	Weight of Toluol displaced.	Water at 40° corresponding to Toluol.	Specific Gravity of $ZnBr_2$ at 20°.
	Grams.	Degrees.	Grams.	Grams.	
(1)	3.8856	19.8	0.7960	0.9206	4.220
(2)	11.2394	20.3	2.303	2.664	4.218
	Average				4.219

The value 4.22 is used in the work which follows. In this connection it may be of interest to compare the specific gravities of the substances recently determined here.

SPECIFIC GRAVITIES COMPARED WITH WATER AT 4°.

Substance.	Old Values.	Former Experiments.	New Values.	Temperature.
Anhydrous $BaCl_2$	3.85	Quincke, Favre and Volson, Schroeder	3.86	24°
$BaBr_2$	4.23	Schiff	4.79	24°
$SrBr_2$	3.96	Bödeker	4.22	24°
$ZnBr_2$	3.64	Bödeker	4.22	20°
Crystallized $BaCl_2 2H_2O$	3.05±	Joule and Playfair, Schiff, Schroeder	3.10	24°

PRELIMINARY ANALYSES OF ZINCIC BROMIDE.

Preparation of Zincic Oxide. The zincic bromide used for the first series of experiments was made by the action of pure hydrobromic acid upon pure zincic oxide. For the preparation of the oxide "pure" zinc of commerce was dissolved in pure dilute sulphuric acid, and the solution was allowed to remain over an excess of the metal for several weeks. The filtered solution was acidified with sulphuric acid, warmed, and treated with well washed hydric sulphide, until a considerable mass of pure white precipitate had formed.

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The strongly smelling filtrate from this zincic sulphide, now freed from all traces of the most usual metallic impurities, was treated with chlorine water to oxidize any iron or manganese which might be present, and precipitated fractionally with pure sodic carbonate. The first fraction of the precipitate containing traces of iron and manganese was thrown away.

After a thorough washing the second fraction, containing most of the zinc, was dissolved in pure nitric acid, keeping the carbonate in excess. After filtration, the addition of a little ammonic carbonate, and another filtration, the greater part of the zinc present was precipitated by means of ammonic carbonate. When it had been subjected to a thorough washing the basic zincic carbonate was ignited in a double platinum crucible over an alcohol lamp. The oxide thus obtained was washed repeatedly with water, for often an impurity which is held by a wet precipitate may be washed out when the precipitate has been partially decomposed or disintegrated by heat. Artus * has observed that the sodic carbonate occluded in the quantitative precipitation of zinc may be easily removed in this way, and the present experience showed that occluded zinc chloride could be washed away with equal ease. The zinc oxide thus obtained was almost white, with a very faint tinge of yellow; upon solution in nitric acid it gave absolutely no opalescence with argentic nitrate. Its method of preparation made the presence of non-volatile impurities almost impossible, for it was precipitated from a solution containing nothing but zinc, nitric acid, and ammonia.

Preparation of Hydrobromic Acid. This substance was made by the action of bromine on water in the presence of phosphorus. The bromine was purified by the well known method of Stas,† having been dissolved in a saturated solution of potassic bromide holding zinc oxide in suspension, and distilled from this solution after long standing. The bromine, thus freed from chlorine and iodine, was collected under water and redistilled. Red phosphorus was now purified by very fine pulverization under water and by repeated washing of the powder with pure water. According to Stas this method removes every trace of chlorine which may be held by the substance. Our own experience has not been uniformly favorable in this respect, but upon this occasion and several others both the qualitative tests for the absence of chlorine and the quantitative analysis of the hydrobromic acid made with the assistance of well washed phosphorus were satisfactory. The bromine

* Berzelius. Jahresbericht, XXIII. 132.
† Mém. Acad. Belg., XLIII. Pt. II. 90, 38.

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was allowed to act upon the phosphorus and water with the usual precautions in an apparatus made wholly of glass. The acid thus formed was distilled in five fractions, of which the first consisted chiefly of water and a trace of bromoform. Only the last fraction of the distillate containing perhaps a third of the bromine taken, was used in the work; and this was redistilled with the further rejection of the first and last portions. The remainder was analyzed quantitively with pure silver in order to test its freedom from chlorine, with very satisfactory results. The silver was prepared, weighed, and dissolved with great care, the precipitate was collected upon a Gooch crucible, and all weighings were reduced to the vacuum standard.

PURITY OF HYDROBROMIC ACID.

No. of Experiment.	Weight of Silver.	Weight of Argentic Bromide.	Per cent of Silver in Argentic Bromide.
(3)	1.86058	3.23884	57.446
(4)	1.72320	2.99983	57.443
	Average		57.444
	Stas found		57.445

Preparation of Zincic Bromide. For experiments 5 and 6 zincic bromide was made by simply dissolving in a platinum dish the pure oxide in the pure acid described above. For experiment 7 similar zincic bromide was sublimed in a wide glass tube in a current of pure dry carbon dioxide. The next experiment, No. 9, was made with similar zincic bromide prepared wholly in glass and not sublimed. A large portion of the substance was then prepared by exact neutralization and evaporation in a platinum dish, a strip of pure zinc was added to precipitate a trace of platinum, — which had been dissolved because of the presence of traces of oxidized nitrogen in the oxide, — and the whole was subjected to crystallization. The mother liquor served for analysis 8, and the pure white crystals for the third series of preliminary determinations (Experiments 10, 11, 12, and 13).

Preparation of Silver. — This substance was prepared by the method described in a recent paper upon the atomic weight of barium.*

Pure argentic chloride was reduced by means of pure sodic hydrate and invert sugar, and the metal was washed and fused in a gas flame

* These Proceedings, XXVIII. 22; XXIX. 64.

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upon charcoal. The lumps thus obtained were dissolved in pure nitric acid and precipitated by electrolysis. The beautiful crystals of electrolytic silver were rapidly fused upon cupels of sugar charcoal * in the flame of illuminating gas, and cooled in a reducing atmosphere. Such silver is essentially identical with the much more carefully prepared metal used in the final experiments, and gives every evidence of being pure within two or three parts in a hundred thousand.† A solution of argentic nitrate through which over fifty grams of such silver had passed by electrolysis, was found upon suitable treatment to yield only half a milligram of baric sulphate; hence the silver could not have contained more than two parts of sulphur in a million.

Preparation of other Materials. — Nitric acid was repeatedly distilled, the last portion of the distillates being used. It is needless to say that it was wholly free from halogens. The sulphuric acid used for analytical purposes was distilled with great care; that used for desiccators was boiled with a little ammonic sulphate. The water used in the preliminary determinations was twice distilled in a tin condenser. In order to avoid the introduction of chlorine, carbon dioxide was prepared at first from acid sodic carbonate and sulphuric acid, later from dilute nitric acid and marble. Nitrogen mixed with argon was prepared by passing a mixture of air and ammonia over red-hot copper. Both gases were very thoroughly washed.

Method of Analysis. — The necessity of driving out every trace of water from the substance to be analyzed was the precaution upon which most labor was expended. The low boiling points of zincic bromide makes it possible to distil the substance easily in a hard glass tube. Accordingly, for the first series of very crude experiments pure zincic bromide was distilled in a tube provided with bulbs, which were sealed off when filled. In order to obviate the introduction of an error from the additional weight of the atmosphere of carbon dioxide in which the distillation took place, the bulbs were heated to about 120° at the moment of sealing. The bulbs were weighed after scratching them upon each end with a file; and after the zinc bromide had been dissolved out the glass was weighed alone. The bromine present was weighed as argentic bromide, and the atomic weight of zincic was calculated from the ratio of argentic and zincic bromides. The more trustworthy results ranged from 65.40 to 65.54, with an average of 65.47; but it was clear that the method admitted of too many possibilities of error to yield satisfactory results.

* These Proceedings, XXIX. 65. † Ibid.

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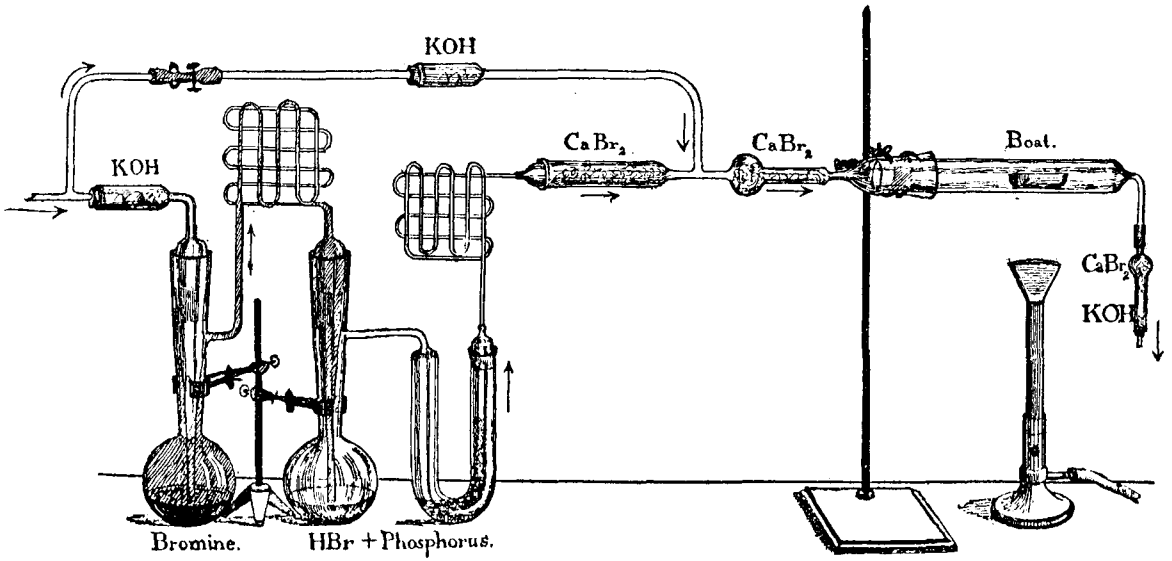

APPARATUS FOR FUSING ZINCIC BROMIDE.

Pure dry nitrogen and argon enter the apparatus through the tube at the left. The arrangement for preparing this mixture is not shown. Upon closing the pinchcock in the upper left hand corner the gases are driven through the flasks and charged with dry hydrobromic acid; upon opening the pinchcock the hydrostatic pressure causes the gases to flow through the upper short cut tube and effectually to sweep out the acid from the fusion tube. This latter tube, containing the boat in which the zincic bromide is fused, is at the right of the figure.

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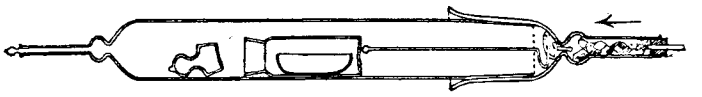
Hence the method which answered well in the recent analysis of strontic bromide* was adopted here. The pure recrystallized or sublimed zincic bromide was placed in a platinum boat and kept for some time in an atmosphere of pure dry nitrogen charged with pure hydrobromic acid. It was found that in this way all the water could be expelled from the salt without the introduction of a trace of oxybromide; indeed, zincic bromide which by rapid heating in the air had been partly decomposed could be speedily brought back to its normal condition by fusion in the atmosphere of dry dilute hydric bromide. The presence of the insoluble oxybromide is easily detected by dissolving the bromide in large amounts of water; in every case the bromide used in the analyses below gave an absolutely clear solution. Baric and strontic bromides ignited in the same way give solutions which are absolutely neutral to methyl orange and phenol phthalein; hence it is most likely than the zincic bromide, which does not admit of similar alkalimetric testing, is also quite normal. For the details the paper upon strontium must be consulted, but a sketch of the apparatus will probably suffice. (See preceding page.) In the present case hydrogen could not be added to the nitrogen for fear of reducing some of the zincic bromide; but no trouble was experienced from corrosion of the boat. When the substance had been kept for some time in a state of tranquil fusion, and had just solidified, the boat was quickly slid into a weighing tube which was in its turn placed in the automatic desiccator tube shown below. After the tube and boat



had been heated to about 200° for some time in a current of pure dry air, the desiccator tube was raised to a vertical position, the stopper being thus allowed to fall into place.

After weighing, the pure zinc bromide was dissolved in water and precipitated by means of a slight excess of very carefully weighed pure silver in very dilute solution. The argentic bromide was collected upon a Gooch crucible, the shreds of asbestos carried through (0.05 to 0.20 milligram) were collected upon a very small fine filter, and the total weight of the argentic bromide thus obtained gave one ratio upon which to base the atomic weight of zinc. In the third series the filtrate

* These Proceedings, XXX. 369.

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was all evaporated to very small bulk, and the excess of silver precipitated by hydrobromic acid and weighed upon a Gooch crucible in the same way as the other portion of argentic bromide. By subtracting this excess from the total silver originally weighed out, the weight of silver equivalent to the zincic bromide could be easily found. Great care was taken to exclude daylight, and to carry out all the precautions necessary in accurate work. The data are given below.

SECOND SERIES.

THE RATIO OF ZINCIC BROMIDE TO ARGENTIC BROMIDE.

No. of Analysis.	Weight of Zincic Bromide.	Weight of Argentic Bromide.	Atomic Weight of Zinc.
	Grams.	Grams.	
(5)	1.69616	2.82805	65.469
(6)	1.98198	3.30450	65.470
(7)	1.70920	2.84949	65.487
(8)	2.35079	3.91941	65.470
(9)	2.66078	4.43751	65.400
	Average		65.459

THIRD SERIES.

THE RATIO OF ZINCIC BROMIDE TO SILVER AND ARGENTIC BROMIDE.

No. of Analysis.	Weight of Zincic Bromide.	Weight of Silver.	Weight of Argentic Bromide.	Atomic Weight of Zinc from $Ag_2 : ZnBr_2$.	Atomic Weight of Zinc from $2AgBr : Zn\ Br_2$.
	Grams.	Grams.	Grams.		
(10)	2.33882	2.24063	3.90067	65.409	65.400
(11)	1.97142	1.88837	3.28742	65.444	65.434
(12)	2.14985	2.05971	3.58539	65.396	65.402
(13)	2.00966	1.92476	3.35074	65.472	65.463
	Average			65.430	65.425

The second series of results, excepting the last determination, is undoubtedly affected by the presence of water in the zincic bromide; for the methods of drying and transference had not been perfected. The third series was much more carefully made, but even here there was a possibility of the retention of a small amount of water in some of the analyses, hence this result also is probably somewhat too high.

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The results of the four analyses of the third series give the following figures for the per cent of silver in the bromide: 57.443, 57.443, 57.447, and 57.443. The mean of these results is 57.444; Stas having found 57.445. It will be remembered that the hydrobromic acid from which the zincic bromide was made gave precisely similar results. This identity proves that the analytical work was without fault, and that argentic bromide does not possess the slightest tendency to occlude zincic bromide when precipitated from dilute solutions. The analysis of the hydrobromic acid proved that the material was free from chlorine and iodine.

Accordingly the rather large variations in the results must be due wholly to the original condition of the samples of zincic bromide. It remained therefore, to make a final series of determinations upon zincic bromide from which water should have been absolutely excluded; and since one of us was unfortunately called away, this series was made by the other alone.

Final Series of Determinations.

By Theodore William Richards.

One determination of the final series, No. 17, was made with the old zincic bromide in the new apparatus. The others were all made from new material prepared from electrolytic zinc and pure bromine, instead of from zincic oxide and hydrobromic acid. The electrolytic zinc was prepared with great care in the following manner: An excess of "pure" zinc was treated with somewhat dilute pure sulphuric acid at 80° until upon dilution a marked amount of basic salt was formed. About three hundred grams of zinc had been dissolved; and this diluted solution was allowed to stand for many hours in contact with the zinc and the basic salt. After filtering, clean pieces of zinc were added to the solution; and no further metallic precipitate formed upon the zinc. The solution was then decanted and treated with a small amount of sulphuric acid and much hydric sulphide. After some time the pure white precipitate was separated by decantation and filtration, and the solution was oxidized by an excess of pure chlorine. To this solution was then added enough very pure sodic carbonate to form a slight precipitate, and the mixture was allowed to stand several days with occasional stirring. The pure white precipitate, which must have contained any trace of iron remaining, was filtered off, and the sulphate of zinc was crystallized three times successively from hot water.

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The solution of the last crystals was allowed to stand for two days over several grams of the purest crystalline electrolytic zinc in a large platinum dish. At the end of that time the solution contained some basic salt, but the dish showed no sign of a metallic coating. The solution was filtered, treated with an excess of freshly distilled ammonia, and electrolyzed. A thin rod of very pure zinc served as the negative pole, and a platinum wire as the positive. Six decomposing cells were run simultaneously on a shunt from a fifty-volt dynamo which was being used for charging a storage battery. The current in each decomposing cell varied from one to one and a half amperes, — if a much stronger current was used the cells became too warm. As Ramsay and Reynolds * have suggested, it is advisable to remove the remarkably beautiful crystals from time to time as they grow; for this purpose a bent five-pronged glass fork made from a heavy rod was found very useful. The crystals were washed with ammonia until the washings were absolutely free from sulphuric acid, then with pure very dilute hydrobromic acid, and finally with much pure water. About forty grams of pure zinc thus formed were treated with an excess of pure bromine, which had been shaken with an alkaline bromide in aqueous solution, dissolved in concentrated calcic bromide, precipitated by water, and distilled under dilute pure hydrobromic acid. The Jena glass flask in which the combination took place was cooled during the reaction. The red solution was filtered in a glass funnel through asbestos, and the excess of bromine, together with any trace of iodine which may have been present, was driven off by leaving the Jena flask upon the steam bath for some time in a very much inclined position. The diluted colorless solution was evaporated to small bulk, and the greater part of it was subjected to fractional crystallization by cooling to zero. A portion which had crystallized twice successively, from water was labelled (A), and another portion, the extreme mother liquor remaining from two crystallizations was labelled (C). Sample (B), the intermediate fraction, was not used in these experiments, as (A) and (C) were proved to be identical.

Before analysis both (A) and (C) were subjected either to distillation or to sublimation. The sublimation was carried on in the lower part of a platinum retort, to which had been fitted closely a glass adapter for conducting the current of pure dry carbon dioxide. The substance to be sublimed was contained in a small platinum crucible fitted with a wire handle, by which it could easily be raised, lowered, or removed.

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* *Loc. cit.*

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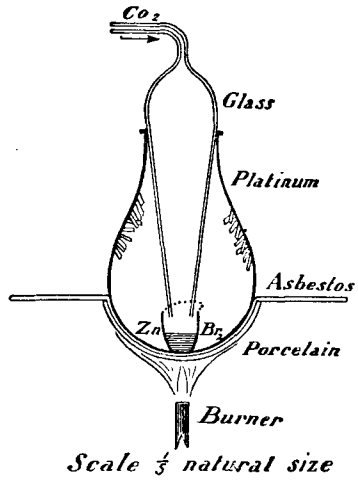
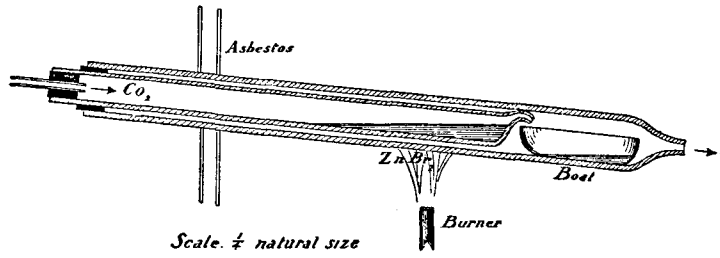
The adapter was so arranged that the current of gas came as closely as possible in contact with the crucible, and so that any zinc bromide which might condense in a liquid form upon the glass, and thus run the risk of taking alkali from it, must return to the crucible and be redistilled. The sectional drawing will give a clearer idea of the arrangement.

Two powerful Bunsen burners supplied heat from below, impinging upon a porcelain dish which fitted closely to the bottom of the retort and protected the platinum. The gases from the flame were diverted by a large diaphragm of asbestos board. By means of this arrangement it is possible to sublime about half a gram of zincic bromide an hour; the crystals are exceedingly beautiful, and give every evidence of great purity.



Scale $\frac{1}{3}$ natural size

Instead of being sublimed, some of the pure salt was distilled in a current of carbon dioxide. For this purpose a medium sized tube of the hardest glass was drawn out so as to serve for a small retort, and this was encased in a larger hard glass tube, from which it was separated by several pieces of platinum foil. A platinum boat, into which was directed the drawn out and turned over point of the inner tube, served as the receiver. Here again a diagram must assist the explanation.



Scale. $\frac{1}{4}$ natural size

The zinc bromide thus distilled possessed a peculiarly brilliant white lustre; in no case did the boat lose or gain the twentieth of a milligram in weight during the distillation.

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The attempt was made also to distil the bromide in a vacuum, but the reduction of the pressure lowered the boiling point too nearly to the proximity of the melting point for convenient manipulation.

In this connection it may be well to state the atomic weight of zinc obtained from these specimens, in order to show their identity. The details of these figures are given later.

From the substance used in the preliminary determinations (Expt. 17)	65.410
From new substance not crystallized from water but distilled in carbon dioxide (Expt. 14)	65.403
From extreme mother liquors from crystallization (C) sublimed in carbon dioxide (Expt. 18)	65.404
From purest crystals (A), twice crystallized from water and sublimed (Expt. 15, 19)	65.404
From purest crystals (A) twice crystallized from water and twice distilled in carbon dioxide (Expt. 16) . . .	65.398
Average . . . . . Zn =	65.404

Silver. — The silver used in the final determinations was repeatedly purified by the methods already described. Finally the beautiful electrolytic crystals were fused in a small crucible of pure lime in a vacuum. In this way the metal may be obtained in the purest possible state, for if it is distilled according to Stas there is always danger of impurity from the oxygen and illuminating gas or hydrogen used in the oxygen blowpipe.

Other Materials. — The acids were purified in the usual fashion and the greater part of the water used was only distilled twice, rejecting the first portions. For experiment 16, all the water used was distilled three times, once over potassic permanganate. Of course the platinum condenser which has been already described served for all of these distillations.*

Phosphoric pentoxide was sublimed in a stream of pure oxygen. Since the presence of oxides of nitrogen in carbon dioxide might assist the partial decomposition of zincic bromide, nitric acid was rejected as a means of decomposing marble, and very dilute hydrochloric acid was used instead. The gas was purified by passing through a solution of sodic hydric carbonate, long tubes containing argentic nitrate, and much pure water. Since the last tube containing water gave absolutely no test for chlorine after over a hundred litres of the gas

* These Proceedings, XXX. 380.

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had passed through it, one may safely assume that the purification was sufficient. The gas was dried by means of sulphuric acid and phosphoric pentoxide.

Method of Analysis. — Perhaps the best method of explaining the method of analysis is to give a detailed description of a single determination; and for this purpose Analyses 15 and 19, in which both silver and argentic bromide were weighed, will best serve.

The very pure sublimed zincic bromide was pressed into a platinum boat; and the boat was placed in a tube of hard glass, which had been ground into another tube designed to contain a weighing bottle. The apparatus consisted essentially of a combination of the two pieces of apparatus shown upon pages 167 and 168; it was devised for a research upon the atomic weight of magnesium now being carried on by Messrs. Richards and Parker, and it will be described in full when that investigation is published. With the help of this apparatus it was possible to heat the zincic bromide to any temperature below its boiling point in an atmosphere of pure dry air, pure dry carbon dioxide, or pure dry carbon dioxide charged with hydrobromic acid; and these gases could be changed at will merely by the opening and closing of stopcocks. When the heating had been continued for the desired length of time, it was possible to push the boat into the weighing bottle and to stopper the weighing bottle very tightly in a perfectly dry atmosphere, without the least chance of the absorption of moisture from the outside air. All the apparatus which could possibly come into contact with bromine or hydrobromic acid was made of glass, with ground glass joints and glass gridirons for convenient refilling.

The zincic bromide was heated very gradually at first in an atmosphere of carbon dioxide which had been dried by passing over sulphuric acid, fused zincic bromide, and phosphorus pentoxide. If heated very gradually in this way, zincic bromide may be almost wholly dehydrated without loss of bromine; but a basic bromide is certain to form if the heating is rapid. When all of the apparent water had been expelled from the substance and its containing tube, dry hydric bromide was added to the carbonic dioxide, and the temperature was gradually raised to the fusing point of zincic bromide. The bromide was kept at a temperature just above its melting point for about an hour; during this time perhaps a tenth of the substance sublimed in the exit end of the "combustion" tube, — rendering the drying tube — which had been ground on to protect the exit — unnecessary. It was assumed that at the end of an hour the fused zincic bromide must be as free from water and from basic salt as it was

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possible to obtain it; accordingly, the temperature was allowed to fall to about 200°, and the current of dry hydrobromic acid was stopped. Soon air — dried by means of sulphuric acid, fused potash, and phosphorus pentoxide — was substituted for the carbon dioxide, the temperature being allowed to fall to about 150° to avoid any possible decomposition of the zincic bromide; and this current of air was continued for several hours until long after every trace of hydrobromic and carbonic acid had been swept away. In order to "make assurance doubly sure" the whole length of the tube, weighing-bottle and all, was heated to 100° or more several times, in order to prevent any possible occlusion of acid. When all was in readiness, the warm boat was pushed by means of a long glass rod into the weighing bottle, and the bottle was stoppered with the help of the same rod. The apparatus was then pulled to pieces, the closed bottle was transferred at once to a tight desiccator, and after a suitable rest of several hours, it was weighed with all possible care. The various weighings are tabulated below.*

	Common Weights Right-hand pan,	Tare · Standard Weights, Left-hand Pan by Substitution.	Standard Weights corrected.
	Grams.	Grams.	Grams.
Weight of boat beforehand .	7.7693	7.76937	7.76932
Weight of boat + bottle . .	19.9757	0.00372	0.00372
The same + $ZnBr_2$ after seven hours' cooling	25.2389	5.26754	5.26747
After two hours more . . .	25.2389	5.26754	5.26747
After two hours' standing in balance	. . . .	5.26757	5.26750
Weight of boat after experiment	7.7693	7.76938	7.76933
Boat + bottle afterward . .	19.9757	0.00375	0.00375
Gain of boat	. . . .	. . . .	0.00001
Gain of boat + bottle . . .	. . . .	. . . .	0.00003
Average tare of boat + bottle + $ZnBr_2$	. . . .	. . . .	5.26748
Average tare of boat + bottle .	. . . .	. . . .	0.00373
Weight of $ZnBr_2$ in air . . .	. . . .	. . . .	5.26375
Correction to vacuum 20° and 762 mm.	. . . .	. . . .	.00074
Weight of $ZnBr_2$ in vacuum .	. . . .	. . . .	5.26449

Before having been treated with water, the bottle and boat were allowed to stand for twenty hours in somewhat moist air. During

* For detailed method see These Proceedings, XXVIII. 5.

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that time they gained only two tenths of a milligram, showing that the diffusion of moisture through the stopper was very slow. In order to prove the efficiency of the drying and fusing apparatus, the bottle with its contents were returned to it, and the stopper was removed by means of a wire while a current of dry air was allowed to pass through the whole apparatus. This current was continued for half an hour, the boat and bottle being warmed to about 120°. After suitable cooling the substance was found to have lost one tenth of a milligram, being one tenth heavier than it was in the first place. These weights were not included above in order to avoid complications; they do not belong necessarily to the analysis, but merely serve to show that the apparatus was wholly sufficient for its purpose.

The boat and its contents were conveyed with great care to a large Bohemian beaker, and the weighing bottle was rinsed out many times with the purest water. When the zincic bromide had wholly dissolved, the perfectly clear solution was transferred through a large funnel to the glass stoppered Erlenmeyer flask intended to serve for the precipitation. The boat was easily washed by allowing it to rest in the funnel, and of course beaker and all were rinsed with the most scrupulous care. The total volume of the thus diluted zincic bromide amounted to about two hundred and fifty cubic centimeters.

The silver to be used for the precipitation weighed 5.04328 grams in the air, or 5.04313 grams in vacuum. It was dissolved in ten cubic centimeters of nitric acid diluted with water in a large flask provided with a bulb tube, and the absolutely clear solution was freed from lower oxides of nitrogen by standing upon the steam bath. The contents of the bulbs, usually containing only a few hundredths of a milligram of silver, were washed back into the flask, and the whole was diluted to about half a litre.

The addition of the argentic nitrate to the zincic bromide took place in the dark-room,* and great pains were taken to prevent exposure of the materials to anything but non-actinic light from this time until the final weighing of the argentic bromide. Of course every trace of silver was washed into the flask containing the zincic bromide. After the whole had been very thoroughly shaken and allowed to stand for several days, 0.21 cubic centimeter of hydrobromic acid (one cubic centimeter was equivalent to a milligram of silver) failed to produce an evident precipitate, even when the solution was lighted by a brilliant condensed beam of yellow light. On the other hand, 0.60 cubic

* See previous papers upon barium and strontium.

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centimeter of an equivalent solution of silver produced an evident cloudiness. 0.40 cubic centimeter more also produced a cloud. Still 0.20 cubic centimeter gave a very faint indication of opalescence, after a long time, and finally 0.21 gave no trace. On titrating back with hydrobromic acid, it was necessary to add 1.21 cubic centimeters more before the point was reached where an extra 0.20 produced no precipitate. The total amount of silver solution added was then 1.41 cubic centimeters, or 0.21 to precipitate the first amount of hydrobromic acid added, 0.21 to show that all the bromine was precipitated, and 0.99 to correspond to the true amount of silver to be added in order to attain the end point; while the total amount of hydrobromic acid added to reach the end point in the other direction was 1.42 cubic centimeters, an amount which must be subtracted from the amount of silver added. Hence, since the true amount of silver corresponding to the zincic bromide is the mean between the amounts found by titrating in opposite directions,* we obtain it as follows: —

AMOUNT OF SILVER REQUIRED.

		Grams in Vacuum.
Titrating with argentic nitrate .	5.04313 + 0.00099	= 5.04412
Titrating with hydrobromic acid	5.04313 + 0.00141 — 0.00142	= 5.04132
Average: silver required		5.04362

Since it is hardly probable that the end point may be obtained by this method more nearly than the tenth of a milligram, the last figure is omitted below.

If, as is probable, the action of silver and hydrobromic acid in preventing the solution of silver bromide resembles the action of silver and hydrochloric in precipitating solutions of silver chloride (Stas), the difference between the end points (1.00 milligram of silver) corresponds to six times the amount of argentic bromide dissolved. That is, this amount must be about $\frac{1.74}{6}$ or 0.29 milligram in 0.85 liter of a solution containing two or three cubic centimeters of nitric acid and about five grams of zincic nitrate.

In order to precipitate all the bromine, four milligrams more of argentic nitrate were added to the solution and the whole was very

* These Proceedings, XXVIII. 24, XXIX. 74, XXX. 384.

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vigorously shaken. After a day or two the mixture was filtered through a weighed Gooch crucible and the precipitate was shaken and allowed to stand with many successive portions of water containing five milligrams of argentic nitrate to the litre. It was finally transferred quantitatively to the crucible, washed with pure water to remove the traces of argentic nitrate and dried at 160° in a porcelain drying oven in a stream of air purified by passing over sulphuric acid and potash. The two litres of filtrate were allowed to stand until the shreds of asbestos had settled; and these were collected upon three thicknesses of the best filter paper, ignited and weighed. The main body of the precipitate was transferred to a porcelain crucible, weighed, fused in a porcelain oven, and weighed again. Below are the data.

	Common Weights.	Standard Weights by Substitution.	Standard Weights corrected.
	Grams.	Grams.	Grams.
Gooch crucible alone	18.4812	0.22840	0.22840
Gooch crucible + AgBr	27.2633	9.01052	9.01050
Argentic bromide in air	. . .	. . . .	8.78210
Correction to vacuum	. . .	. . . .	0.00039
Chief mass of argentic bromide in vacuum	. . .	. . . .	8.78249
Porcelain crucible + AgBr	25.6757	8.37781	
The same after fusion	25.6755	8.37760	
Loss on fusion	. . .	0.00021	0.00021
Crucible + ash + asbestos	15.2857	0.05284	
Crucible	15.2853	0.05226	
Ash + asbestos	. . .	0.00058	
Ash of three filters	. . .	0.00012	
Asbestos	. . .	0.00046	0.00046
Total weight of AgBr	. . .	. . . .	8.78274
Subtract amount corresponding to 1.42 + 0.20 = 1.62 c.c. HBr solution	. . .	. . . .	0.00282
Argentic bromide corresponding to zincic bromide	. . .	. . . .	8.77992

Thus 5.26449 grams of zincic bromide correspond to 5.0436 grams of silver and 8.77992 grams of argentic bromide. If bromine and silver are taken as 79.955 and 107.93 as usual, the atomic weights of zinc computed from these ratios are identical, — 65.404. Since this is the case, of course the per cent of silver found in argentic bromide $\frac{5.0436}{8.77992} \times 100$ is identical with that obtained by Stas, or 57.445.

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In no one of the other determinations were both silver and argentic bromide determined, hence the others were simpler in execution, although essentially the same in principle. The end point in analysis 17 was probably not determined more nearly than two tenths of a milligram, while that in analysis 19 was determined by the nephelometer * much more accurately even than in the detailed determination. Indeed this value was so accurate that the hundredths of a milligram may have some significance, although the weights taken were so large. The data of all these final determinations are given below.

FINAL DETERMINATIONS.

The Ratio of Zincic Bromide to Silver.

Number of Analysis.	Weight of Zincic Bromide.	Weight of Silver.	Ratio. $\frac{ZnBr_2}{2Ag}$.	Atomic Weight of Zinc.
	Grams.	Grams.		
(14)	6.23833	5.9766	104.379	65.403
(15)	5.26449	5.0436	104.380	65.404
(16)	9.36283	8.9702	104.377	65.398
	Average		104.379	65.402

The Ratio of Zincic Bromide to Argentic Bromide.

Number of Analysis.	Weight of Zincic Bromide.	Weight of Argentic Bromide.	Ratio. $\frac{ZnBr_2}{2AgBr}$.	Atomic Weight of Zinc.
	Grams.	Grams.		
(17)	2.65847	4.43358	0.599622	65.410
(18)	2.30939	3.85149	0.599606	65.404
(19)	5.26449	8.77992	0.599606	65.404
	Average		0.599611	65.406

From the first ratio, if $O = 16$ $\quad Zn = \mathbf{65.402}$

From the second ratio, if $O = 16$ $\quad Zn = \mathbf{65.406}$

Average, if $O = 16$ $\quad Zn = \mathbf{65.404}$

If $O = 15.96$ $\quad Zn = \overline{65.240}$

If $O = 15.88$ $\quad Zn = 64.912$

* These Proceedings, XXX. 385.

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In this determination the only serious possibility of error is that the zincic bromide may have contained a lingering trace of water in spite of the elaborate precautions adopted to secure its absence. It is hoped that before long a determination of the zinc as well as of the bromine in zincic bromide may be made in this laboratory, furnishing evidence upon this point. However, since the figure given above agrees closely with the probable corrected result of Morse and Burton's investigation, as well as with the somewhat incomplete determinations of Baubigny and Gladstone and Hibbert, the value 65.40 may be safely adopted for the present as the most probable value of the atomic weight of zinc.

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IX.

NOTE ON THE AUTOMORPHIC LINEAR TRANSFORMATION OF A BILINEAR FORM.

By Henry Taber.

Presented April 10, 1895.

§ 1.

In the *Bulletin of the New York Mathematical Society* for July, 1894, I have shown that not every proper orthogonal substitution can be generated by the repetition of an infinitesimal orthogonal substitution. That is to say, if we designate a substitution of the orthogonal group as of the first or second kind according as it is or is not the second power of a substitution of the group, there are then proper orthogonal substitutions of the second kind; and whereas any substitution of the first kind can be generated by the repetition of an infinitesimal substitution of the group, no substitution of the second kind can be generated thus. Nevertheless, by the repetition of an infinitesimal substitution of the orthogonal group, we can obtain a substitution of the first kind which shall be as nearly as we please equal to any proper substitution whatever of the second kind.

I also pointed out in this paper that for the orthogonal group every substitution of the first kind was the mth power of a substitution of the group, for any positive integer m; and that every substitution of the second kind was the $(2m+1)$th power of a substitution of the group.

It follows of course at once that an exactly similar theory exists for the group of linear substitutions which transform automorphically a symmetric bilinear form with cogrediant variables. An exactly similar theory exists also for the group of linear substitutions which transform automorphically an alternate bilinear form with cogrediant variables, and for the group of linear substitutions which transform automorphically a general bilinear form (neither symmetric nor alternate) with cogrediant variables, as remarked in a note at the conclusion of the above mentioned article.

On the other hand, any linear substitution of the group of linear substitutions which transform automorphically a bilinear form with

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contragrediant variables can be generated by the repetition of an infinitesimal substitution of the group. For, if the two sets of variables of the bilinear form

$$(\Omega \,|\!|\, x_1, x_2, \ldots x_n \,|\!|\, y_1, y_2, \ldots y_n)$$

are contragrediant, and if

$$(x_1, x_2, \ldots x_n) = (\phi \,|\!|\, \xi_1, \xi_2, \ldots \xi_n),$$

$$(\eta_1, \eta_2, \ldots \eta_n) = (\breve{\phi} \,|\!|\, y_1, y_2, \ldots y_n),$$

in which $\breve{\phi}$ denotes the transverse or conjugate to ϕ, we have

$$(\phi^{-1}\,\Omega\,\phi \,|\!|\, \xi_1, \xi_2, \ldots \xi_n \,|\!|\, \eta_1, \eta_2, \ldots \eta_n) = (\Omega \,|\!|\, x_1, x_2, \ldots x_n \,|\!|\, y_1, y_2, \ldots y_n);$$

and the necessary and sufficient condition that the transformation shall be automorphic is

$$\phi^{-1}\,\Omega\,\phi = \Omega,$$

or

$$\Omega\,\phi = \phi\,\Omega.*$$

Let now δ denote the identical substitution. Since it is assumed that a reciprocal of ϕ exists, that is, $|\phi| \neq 0$, a polynomial $\chi = f(\phi)$ in ϕ can be found such that

$$\phi = e^{\chi},$$

---

* In this paper I employ the notation of Cayley's "Memoir on the Linear Automorphic Transformation of a Bipartite Quadric Function," *Philosophical Transactions*, 1858, with these exceptions, namely, the identical substitution will be denoted by δ, and the linear substitution or matrix transverse or conjugate to the linear substitution or matrix ϕ will be denoted by $\breve{\phi}$. Cayley denotes the bilinear form $\Sigma_r \Sigma_s a_{rs} x_s y_r$ $(r, s = 1, 2, \ldots n)$, as above, by

$$(\Omega \,|\!|\, x_1, x_2, \ldots x_n \,|\!|\, y_1, y_2, \ldots y_n),$$

the symbol Ω denoting the matrix

$$\begin{matrix} a_{11}\, a_{12} \ldots \\ a_{21}\, a_{22} \ldots \\ \ldots\ldots \end{matrix}$$

that is, the square array of coefficients of the form.

The determinant of the linear substitution ϕ will be denoted by $|\phi|$.

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where e^{χ} denotes the convergent infinite series

$$\delta + \chi + \frac{1}{2}\chi^2 + \frac{1}{3!}\chi^3 + \cdots + \frac{1}{m!}\chi^m + \cdots *$$

Since ϕ is commutative with Ω, χ is also commutative with Ω; consequently for any positive integer m, $\frac{1}{m}\chi$ and therefore $e^{\frac{1}{m}\chi}$ are commutative with Ω. Whence it follows that if

$$\psi = e^{\frac{1}{m}\chi},$$

we have

$$\psi^{-1}\,\Omega\,\psi = \Omega,$$

and

$$\psi^m = e^{\chi} = \phi.$$

That is, any linear substitution which transforms automorphically the bilinear form

$$(\Omega \setminus x_1, x_2, \ldots x_n \setminus y_1, y_2, \ldots y_n)$$

with contragrediant variables is the mth power of a linear substitution which also transforms this form automorphically. By taking m sufficiently great, the coefficients of the linear substitution χ can be made as nearly as we please equal to zero, and thus the linear substitution $\psi = e^{\frac{1}{m}\chi}$ may be made as nearly as we please equal to the identical substitution. But however great m may be, we have, nevertheless,

---

* The infinite series

$$e^{\chi} = \delta + \chi + \frac{1}{2}\chi^2 + \frac{1}{3!}\chi^3 + \cdots + \frac{1}{m!}\chi^m + \cdots$$

is convergent for any linear substitution χ; and we have

$$(e^{\chi})^{-1} = e^{-\chi},$$

$$(\widetilde{e^{\chi}}) = e^{\breve{\chi}},$$

and if m is any positive integer,

$$(e^{\chi})^m = e^{m\chi}.$$

If χ and χ' are commutative, we also have

$$e^{\chi}\,e^{\chi'} = e^{\chi+\chi'}.$$

For any linear substitution ϕ whose determinant is not zero a polynomial $\chi = f(\phi)$ in ϕ can be found such that

$$\phi = e^{\chi}.$$

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$$\psi^{-1}\,\Omega\,\psi = \Omega,$$
$$\psi^{m} = \phi;$$

whence it follows that any linear substitution of the group of linear substitutions which transform automorphically a bilinear form with contragrediant variables can be generated by the repetition of an infinitesimal substitution of the group.

§ 2.

If the two sets of variables of the bilinear form

$$(\Omega \,|\!|\, x_1, x_2, \ldots x_n \,|\!|\, y_1, y_2, \ldots y_n)$$

are transformed by linear substitutions transverse or conjugate to each other, so that

$$(x_1, x_2, \ldots x_n) = (\phi \,|\!|\, \xi_1, \xi_2, \ldots \xi_n),$$
$$(y_1, y_2, \ldots y_n) = (\breve{\phi} \,|\!|\, \eta_1, \eta_2, \ldots \eta_n),$$

where $\breve{\phi}$ denotes the linear substitution transverse or conjugate to ϕ, we have

$$(\phi\,\Omega\,\phi \,|\!|\, \xi_1, \xi_2, \ldots \xi_n \,|\!|\, \eta_1, \eta_2, \ldots \eta_n)$$
$$= (\Omega \,|\!|\, x_1, x_2, \ldots x_n \,|\!|\, y_1, y_2, \ldots y_n).$$

The necessary and sufficient condition that this transformation shall be automorphic is that ϕ shall satisfy the equation

$$\phi\,\Omega\,\phi = \Omega.$$

The class of linear substitutions that satisfy this equation, that is, the linear substitutions which transform the bilinear form in the manner described, do not form a group; but they can be separated into substitutions of the first or second kind according as they are or are not the second power of a substitution of this class.* And any substitution of the first kind can then be generated by the repetition of an infinitesimal substitution of this class, whereas no substitution of the second kind can be generated thus.

* If $\phi\,\Omega\,\phi = \Omega$, then $\phi^2\,\Omega\,\phi^2 = \phi\,(\phi\,\Omega\,\phi)\,\phi = \phi\,\Omega\,\phi = \Omega$.

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For assuming that the determinant of the form is not zero, that is, $|\Omega| \neq 0$, it follows that $|\phi| \neq 0$. Consequently a polynomial $\chi = f(\phi)$ can be found such that

$$\phi = e^{\chi}.*$$

Let

$$\vartheta = f(\phi)\,\Omega^{-1},$$

then

$$\phi = e^{\vartheta\,\Omega}.$$

From the identity

$$e^{-\Omega\,\vartheta}\,\Omega\,e^{\vartheta\,\Omega} = \Omega\,\dagger$$

we have also

$$\phi = e^{-\Omega\vartheta} = \left(e^{\Omega\,\vartheta}\right)^{-1}.$$

Since

$$\phi^{-1} = \Omega\,\phi\,\Omega^{-1},$$

therefore

$$\Omega\,\vartheta = \Omega\,(\vartheta\,\Omega)\,\Omega^{-1} = \Omega f(\phi)\,\Omega^{-1} = f(\Omega\,\phi\,\Omega^{-1}) = f(\phi^{-1})\ \ddagger$$

is a polynomial in ϕ, and consequently commutative with $\vartheta\,\Omega$. Whence we have *

$$e^{\vartheta\,\Omega + \Omega\,\vartheta} = e^{\vartheta\,\Omega}\,e^{\Omega\,\vartheta} = \phi\,\phi^{-1} = \delta.$$

Conversely, if $\vartheta\,\Omega$ and $\Omega\,\vartheta$ are commutative and such that

$$e^{\vartheta\,\Omega + \Omega\,\vartheta} = \delta,$$

then if

$$\phi = e^{\vartheta\,\Omega},$$

from the preceding identity it follows that

$$\phi\,\Omega\,\phi = \Omega.$$

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* See note, page 183.

† For any positive integer m we have

$$\Omega\,(\vartheta\,\Omega)^m = (\Omega\,\vartheta)^m\,\Omega.$$

Therefore

$$e^{-\Omega\,\vartheta}\,.\Omega\,e^{\vartheta\,\Omega} = e^{-\Omega\,\vartheta}\,.\,e^{\Omega\,\vartheta}\,.\,\Omega = \Omega.$$

‡ Since

$$f(\phi) = \Sigma_m\,c_m\,\phi^m,$$

$$\Omega f(\phi)\,\Omega^{-1} = \Omega\,(\Sigma_m\,c_m\,\phi^m)\,\Omega^{-1} = \Sigma_m\,c_m\,\Omega\,\phi^m\,\Omega^{-1} = \Sigma_m\,c_m\,(\Omega\,\phi\,\Omega^{-1})^m$$
$$= \Sigma_m\,c_m\,(\phi^{-1})^m = f(\phi^{-1}).$$

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In particular, if $\vartheta\,\Omega = -\,\Omega\,\vartheta$, $\phi = e^{\vartheta\,\Omega}$ satisfies the preceding equation.

Let now

$$\theta_0\,\Omega = \tfrac{1}{2}\,(\vartheta\,\Omega + \Omega\,\vartheta) = \tfrac{1}{2}\,\big(f(\phi) + f(\phi^{-1})\big),$$

then

$$\begin{aligned}\Omega\,\theta_0 &= \tfrac{1}{2}\,\Omega\,(\vartheta\,\Omega + \Omega\,\vartheta)\,\Omega^{-1}\\ &= \tfrac{1}{2}\,\big(\Omega f(\phi)\,\Omega^{-1} + \Omega f(\phi^{-1})\,\Omega^{-1}\big)\\ &= \tfrac{1}{2}\,\big(f(\Omega\,\phi\,\Omega^{-1}) + f(\Omega\,\phi^{-1}\,\Omega^{-1})\big)\\ &= \tfrac{1}{2}\,\big(f(\phi^{-1}) + f(\phi)\big) = \theta_0\,\Omega.*\end{aligned}$$

Again, let

$$\theta_1\,\Omega = \tfrac{1}{2}\,(\vartheta\,\Omega - \Omega\,\vartheta) = \tfrac{1}{2}\,\big(f(\phi) - f(\phi^{-1})\big);$$

then

$$\begin{aligned}\Omega\,\theta_1 &= \tfrac{1}{2}\,\Omega\,\big(f(\phi) - f(\phi^{-1})\big)\,\Omega^{-1}\\ &= \tfrac{1}{2}\,\big(\Omega f(\phi)\,\Omega^{-1} - \Omega f(\phi^{-1})\,\Omega^{-1}\big)\\ &= \tfrac{1}{2}\,\big(f(\Omega\,\phi\,\Omega^{-1}) - f(\Omega\,\phi^{-1}\,\Omega^{-1})\big)\\ &= \tfrac{1}{2}\,\big(f(\phi^{-1}) - f(\phi)\big) = -\,\theta_1\,\Omega.\end{aligned}$$

Since $\theta_0\,\Omega$ and $\theta_1\,\Omega$ are polynomials in ϕ, they are commutative. Therefore

$$\phi^2 = e^{2\,\vartheta\,\Omega} = e^{2\,\theta_0\,\Omega + 2\,\theta_1\,\Omega} = e^{2\,\theta_0\,\Omega}\,e^{2\,\theta_1\,\Omega} = e^{2\,\theta_1\,\Omega},$$

since

$$e^{2\,\theta_0\,\Omega} = e^{\vartheta\,\Omega + \Omega\,\vartheta} = \delta.$$

If now

$$\psi = e^{\frac{2}{m}\,\theta_1\,\Omega} = e^{-\,\frac{2}{m}\,\Omega\,\theta_1},$$

$$\psi\,\Omega\,\psi = e^{-\,\frac{2}{m}\,\Omega\,\theta_1}\,\Omega\,e^{\frac{2}{m}\,\theta_1\,\Omega} = \Omega,$$

and

$$\psi^m = \Big(e^{\frac{2}{m}\,\theta_1\,\Omega}\Big)^m = e^{2\,\theta_1\,\Omega} = \phi^2.$$

Consequently, any linear substitution, as ϕ^2, which is the second power of a linear substitution satisfying the equation

$$\phi\,\Omega\,\phi = \Omega,$$

is the mth power for any positive integer m of a solution of this equation. By taking m sufficiently great, we can make the coefficients

* See last note, page 185.

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of $\frac{2}{m}\theta_1\Omega$ as small as we please, and thus we may make the substitution ψ as nearly as we please equal to the identical substitution. Whence it follows that any linear substitution of the first kind which satisfies the equation

$$\phi\,\Omega\,\phi = \Omega$$

(that is, any linear substitution which is the second power of a solution of this equation) can be generated by the repetition of a linear substitution which is also a solution of this equation and which is infinitely near the identical substitution.

Any linear substitution ϕ satisfying the equation

$$\phi\,\Omega\,\phi = \Omega$$

is of the first kind if -1 is not a root of the characteristic equation of ϕ (that is, ϕ is then the second power of a substitution satisfying this equation). For if -1 is not a root of the characteristic equation of ϕ, we may put

$$\Omega^{-1}\Upsilon = -\delta + 2(\delta+\phi)^{-1} = (\delta-\phi)(\delta+\phi)^{-1};$$

and we then have

$$\begin{aligned}
\Upsilon\,\Omega^{-1} &= \Omega\,(\Omega^{-1}\Upsilon)\,\Omega^{-1}\\
&= \Omega\,(\delta-\phi)(\delta+\phi)^{-1}\Omega^{-1}\\
&= \Omega\,(\delta-\phi)\,\Omega^{-1}\cdot\Omega\,(\delta+\phi)^{-1}\Omega^{-1}\\
&= (\delta-\Omega\phi\,\Omega^{-1})(\delta+\Omega\phi\,\Omega^{-1})^{-1}\\
&= (\delta-\phi^{-1})(\delta+\phi^{-1})^{-1}\\
&= (\phi-\delta)(\phi+\delta)^{-1} = -\Omega^{-1}\Upsilon.
\end{aligned}$$

From the expression for $\Omega^{-1}\Upsilon$ we also obtain

$$(\Omega^{-1}\Upsilon+\delta)(\phi+\delta) = 2\delta;$$

and consequently, since $|\,\Omega^{-1}\Upsilon+\delta\,| \neq 0$,

$$\phi = -\delta + 2(\delta+\Omega^{-1}\Upsilon)^{-1} = (\delta+\Omega^{-1}\Upsilon)^{-1}(\delta-\Omega^{-1}\Upsilon).$$

If now $\vartheta = f(\Omega^{-1}\Upsilon)$ is a polynomial in $\Omega^{-1}\Upsilon$ such that

$$\delta+\Omega^{-1}\Upsilon = e^{\vartheta},$$

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then, if $\vartheta' = f(-\Omega^{-1}\Upsilon)$ we have

$$\delta - \Omega^{-1}\Upsilon = e^{\vartheta'};*$$

and consequently

$$\phi = (e^{\vartheta})^{-1} e^{\vartheta'} = e^{-\vartheta+\vartheta'}.$$

Wherefore, if

$$\begin{aligned}
\theta\Omega &= -\vartheta + \vartheta' = -f(\Omega^{-1}\Upsilon) + f(-\Omega^{-1}\Upsilon),\\
\Omega\theta &= \Omega\left(-f(\Omega^{-1}\Upsilon) + f(-\Omega^{-1}\Upsilon)\right)\Omega^{-1}\\
&= -\Omega f(\Omega^{-1}\Upsilon)\,\Omega^{-1} + \Omega f(-\Omega^{-1}\Upsilon)\,\Omega^{-1}\\
&= -f(\Upsilon\Omega^{-1}) + f(-\Upsilon\Omega^{-1})\\
&= -f(-\Omega^{-1}\Upsilon) + f(\Omega^{-1}\Upsilon) = -\theta\Omega;
\end{aligned}$$

and consequently, if

$$\psi = e^{\frac{1}{2}\theta\Omega} = e^{-\frac{1}{2}\Omega\theta},$$

we have

$$\psi\,\Omega\,\psi = \Omega,$$

and

$$\psi^2 = e^{\theta\Omega} = e^{-\vartheta+\vartheta'} = \phi;$$

that is, ϕ is the second power of a solution of the equation

$$\phi\,\Omega\,\phi = \Omega.$$

If a linear substitution satisfying this equation is sufficiently near to the identical substitution, -1 is not a root of its characteristic equation. Therefore an infinitesimal substitution satisfying this equation is of the first kind. But the repetition of a substitution of the first kind gives a substitution of that kind. Whence it follows that no substitution of the second kind, which satisfies the equation, can be

---

* For

$$\begin{aligned}
\vartheta' &= f(-\Omega^{-1}\Upsilon)\\
&= f(\Upsilon\Omega^{-1})\\
&= f(\Omega\cdot\Omega^{-1}\Upsilon\cdot\Omega^{-1})\\
&= \Omega f(\Omega^{-1}\Upsilon)\,\Omega^{-1} = \Omega\vartheta\Omega^{-1}.
\end{aligned}$$

Therefore,

$$\begin{aligned}
e^{\vartheta'} &= e^{\Omega\vartheta\Omega^{-1}}\\
&= \Omega e^{\vartheta}\Omega^{-1}\\
&= \Omega(\delta + \Omega^{-1}\Upsilon)\,\Omega^{-1}\\
&= \delta + \Upsilon\Omega^{-1} = \delta - \Omega^{-1}\Upsilon.
\end{aligned}$$

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generated by the repetition of an infinitesimal substitution satisfying this equation.

Let ϕ be a linear substitution of the first kind of the class we are now considering. That is, let

$$\psi\,\Omega\,\psi = \Omega,$$

and let

$$\phi = \psi^2.$$

The roots of the characteristic equation of ϕ are then the squares of the roots of the characteristic equation of ψ. Consequently, if -1 is a root of the characteristic equation of ϕ, $\sqrt{-1}$ is a root of the characteristic equation of ψ; that is,

$$|\,\psi - \sqrt{-1}\,\delta\,| = 0.$$

But then

$$|\,\psi^{-1} - \sqrt{-1}\,\delta\,| = |\,\Omega\,(\psi^{-1} - \sqrt{-1}\,\delta)\,\Omega^{-1}\,| = |\,\psi - \sqrt{-1}\,\delta\,| = 0;$$

and since

$$\psi^{-1} - \sqrt{-1}\,\delta = -\sqrt{-1}\,\psi^{-1}\,(\psi + \sqrt{-1}\,\delta),$$

we have

$$|\,\psi + \sqrt{-1}\,\delta\,| = 0;$$

that is, $-\sqrt{-1}$ is then also a root of the characteristic equation of ψ. It is convenient at this point to introduce a term which has been employed by Sylvester. Thus, following Sylvester, I shall say that the *nullity* of the linear substitution Φ is m, if all the $(m-1)$th minors of the matrix or determinant of Φ are zero, (that is, the minors of order $n - m + 1$, if n is the number of variables,) but not all the mth minors (the minors of order $n-m$). If now the nullity of $\psi - \sqrt{-1}\,\delta$ is m, then, since

$$\psi - \sqrt{-1}\,\delta = \Omega\,(\psi^{-1} - \sqrt{-1}\,\delta)\,\Omega^{-1},$$

the nullity of

$$-\sqrt{-1}\,\psi^{-1}\,(\psi + \sqrt{-1}\,\delta) = \psi^{-1} - \sqrt{-1}\,\delta$$

is also m; therefore, since $|\,\psi^{-1}\,| \neq 0$, the nullity of $\psi + \sqrt{-1}\,\delta$ is m. Whence, by the "corollary of the law of nullity," the nullity of

$$\phi + \delta = (\psi - \sqrt{-1}\,\delta)\,(\psi + \sqrt{-1}\,\delta)$$

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is then $2m$. Similarly, if p is any positive integer, and if the nullity of

$$(\psi - \sqrt{-1}\,\delta)^p = \Omega\,(\psi^{-1} - \sqrt{-1}\,\delta)^p\,\Omega^{-1}$$

is m, the nullity of

$$(-\sqrt{-1}\,\psi^{-1})^p\,(\psi + \sqrt{-1}\,\delta)^p = (\psi^{-1} - \sqrt{-1}\,\delta)^p$$

is also m; and therefore the nullity of $(\psi + \sqrt{-1}\,\delta)^p$ is m. But then the nullity of

$$(\phi + \delta)^p = (\psi - \sqrt{-1}\,\delta)^p\,(\psi + \sqrt{-1}\,\delta)^p$$

is $2m$.

We have therefore the following theorem by which we may ascertain the existence of substitutions of the second kind. If ϕ is a linear substitution of the first kind which satisfies the equation

$$\phi\,\Omega\,\phi = \Omega,$$

then if -1 is a root of the characteristic equation of ϕ, the nullity of any positive integer power of $\phi + \delta$ is even.

That substitutions of the second kind actually exist may be shown by considering the form

$$a\,(x_1\,y_1 - x_2\,y_2) + b\,x_2\,y_1,$$

which is transformed automorphically if we impose upon the x's the substitution whose matrix is

$$\begin{matrix} -1 & 1 \\ 0 & -1 \end{matrix}$$

and upon the y's the transverse substitution; that is, if we put

$$x_1 = -\xi_1 + \xi_2, \qquad x_2 = -\xi_2,$$

and

$$y_1 = -\eta_1, \qquad y_2 = \eta_1 - \eta_2.$$

This linear substitution does not satisfy the preceding conditions, and is therefore of the second kind. It follows that there are one or more bilinear forms for any number of variables which are transformed automorphically in the manner we have considered in this section by linear substitution of the second kind.

By definition, no solution of the second kind of the equation

$$\phi\,\Omega\,\phi = \Omega$$

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in an even power of a solution of this equation. But if ϕ is a solution of the second kind, for any positive integer m, we can find a linear substitution satisfying this equation whose $(2m+1)$th power is equal to ϕ. Thus, employing the notation of pages 185, 186, let $\vartheta\,\Omega$ be a polynomial in ϕ such that

$$\phi = e^{\vartheta\,\Omega};$$

and, as above, let

$$\theta_0\,\Omega = \tfrac{1}{2}\,(\vartheta\,\Omega + \Omega\,\vartheta), \qquad \theta_1\,\Omega = \tfrac{1}{2}\,(\vartheta\,\Omega - \Omega\,\vartheta).$$

Then, if

$$\psi = e^{\theta_0\,\Omega + \frac{1}{2m+1}\theta_1\,\Omega},$$

$$\psi\,\Omega\,\psi = \Omega,$$

and

$$\psi^{2m+1} = \phi.$$

Corresponding to any linear substitution ϕ of the second kind satisfying the equation

$$\phi\,\Omega\,\phi = \Omega,$$

can always be found a solution ϕ_ζ of the first kind whose coefficients are rational functions of a parameter ζ, such that, by taking ζ sufficiently small, the coefficients of ϕ_ζ may be made as nearly as we please equal to the corresponding coefficients of ϕ.

§ 3.

If the two sets of variables of the bilinear form

$$(\Omega \,|\, x_1, x_2, \ldots x_n \,|\, y_1, y_2, \ldots y_n),$$

of non-zero determinant, are transformed by a linear substitution whose product is equal to the identical substitution; thus, if

$$(x_1, x_2, \ldots x_n) = (\phi \,|\, \xi_1, \xi_2, \ldots \xi_n),$$

$$(y_1, y_2, \ldots y_n) = (\phi^{-1} \,|\, \eta_1, \eta_2, \ldots \eta_n),$$

we have

$$(\breve{\phi}^{-1}\,\Omega\,\phi \,|\, \xi_1, \xi_2, \ldots \xi_n \,|\, \eta_1, \eta_2, \ldots \eta_n)$$

$$= (\Omega \,|\, x_1, x_2, \ldots x_n \,|\, y_1, y_2, \ldots y_n);$$

and the necessary and sufficient condition that the transformation shall be automorphic is

$$\breve{\phi}^{-1}\,\Omega\,\phi = \Omega.$$

Any one of the class of linear substitutions which satisfy this equation is the mth power of a linear substitution of this class, and can be

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generated by the repetition of an infinitesimal substitution of this class. For let $\chi = f(\phi)$ be a polynomial in ϕ such that

$$\phi = e^{\chi}.*$$

Let

$$\vartheta = f(\phi)\,\Omega^{-1},$$

that is,

$$\vartheta\,\Omega = f(\phi);$$

then

$$\breve{\Omega}\,\breve{\vartheta} = f(\breve{\phi}).$$

And since

$$\phi = \Omega^{-1}\,\breve{\phi}\,\Omega,$$

and consequently

$$\breve{\phi} = \breve{\Omega}\,\phi\,\breve{\Omega}^{-1},$$

we have

$$\breve{\Omega}\,\breve{\vartheta} = f(\breve{\Omega}\,\phi\,\breve{\Omega}^{-1}) = \breve{\Omega}\cdot f(\phi)\cdot\breve{\Omega}^{-1}.$$

Therefore

$$\breve{\vartheta}\,\breve{\Omega} = f(\phi) = \vartheta\,\Omega.$$

If now m is any positive integer, and

$$\psi = e^{\frac{1}{m}\vartheta\,\Omega} = e^{\frac{1}{m}\breve{\vartheta}\,\breve{\Omega}},$$

then

$$\breve{\psi} = e^{\frac{1}{m}\breve{\Omega}\,\breve{\vartheta}} = e^{\frac{1}{m}\Omega\,\vartheta},$$

$$\breve{\psi}^{-1} = e^{-\frac{1}{m}\breve{\Omega}\,\breve{\vartheta}} = e^{-\frac{1}{m}\Omega\,\vartheta};$$

and we have identically

$$\breve{\psi}^{-1}\,\Omega\,\psi = e^{-\frac{1}{m}\Omega\,\vartheta}\;\Omega\,e^{\frac{1}{m}\vartheta\,\Omega} = \Omega.$$

We also have

$$\psi^m = e^{\vartheta\,\Omega} = \phi.$$

Consequently any linear substitution ϕ which satisfies the equation

$$\breve{\phi}^{-1}\,\Omega\,\phi = \Omega$$

is the mth power for any positive integer m of a linear substitution ψ which also satisfies this equation; and since by taking m sufficiently great we can make ψ as nearly as we please equal to the identical substitution, ϕ can be generated by the repetition of an infinitesimal substitution which also satisfies this equation.

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* See note, page 183.

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X.

CONTRIBUTIONS FROM THE PHYSICAL LABORATORY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.

XLIV. — THERMO-ELECTRIC INTERPOLATION FORMULÆ.

By Silas W. Holman.

Presented November 13, 1895.

In this paper are collected the several well known types of formulæ for expressing the thermal electro-motive force of a couple as a function of the temperature of its junctions. Two new formulæ are also proposed. All then are tested against the most reliable experimental data upon the subject, and their relative merits discussed.

The Existing Formulæ.

Consider a simple closed electric circuit composed of two different metals, each homogeneous in matter and temper, the metals being in contact at two points. For simplicity, assume the metals to be in the form of wires joined at their ends. Let one junction be at a temperature of $h°$, the other of $c°$, on the ordinary centigrade scale. Let $\Sigma_e^h e$ be employed as a suggestive symbol to denote the resultant electro-motive force in the circuit, induction being excluded from consideration. Then $\Sigma_c^h e$ is a function of h and c which involves constants dependent upon the nature of the metals, and which may be represented by

$$\Sigma_c^h e = f(h, c).$$

The discovery of the natural expression for $f(h, c)$ is not only of scientific importance, but is urgently needed in the development of the art of pyrometry. At present even a satisfactory empirical formula for interpolation is lacking, the best still being probably that of Avenarius and Tait.

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The existing formulæ are the five following.

Ordinary or parabolic:

$$\Sigma_0^t e = at + bt^2 + ct^3 + \ldots\ldots \qquad (1)$$

This is, of course, merely a series in ascending powers of t, where one junction is at any temperature $t°$ C., and the other at 0° C., a, b, and c being constants. A more general form for the case where the cold junction is at any constant temperature, $t_1°$, is

$$\Sigma_{t_1}^t e = a\,(t - t_1) + b\,(t^2 - t_1^2) + c\,(t^3 - t_1^3) + \ldots\ldots$$

These expressions may, of course, be inverted, giving t as a function of Σe.

Avenarius

$$\Sigma_c^h e = (h - c)\,\{a + b\,(h + c)\}, \qquad (2)$$

in accordance with the foregoing notation.

Thomson:

$$\Sigma_c^h e = a\,(\tau_h - \tau_c)\left\{\tau_n - \frac{\tau_h + \tau_c}{2}\right\}, \qquad (3)$$

where τ is the absolute temperature, τ_n being that of the "neutral point."

Tait:

$$\Sigma_0^h e = (k' - k)\,(\tau_h - \tau_c)\left\{\tau_n - \frac{\tau_h + \tau_c}{2}\right\}. \qquad (4)$$

Both of the last two, by the substitution of $t + 273$ for τ obviously reduce to the Avenarius form.

Barus:

$$e_h + e_c = 10^{P + Qh} + 10^{P' + Q'c}. \qquad (5)$$

where e_h represents the thermal emf. of the hot junction and e_c that of the cold junction. In view, however, of the existence of the Thomson effect, these symbols can strictly be interpreted only as having the meaning that $e_h - e_c = \Sigma_c^h e$.

Note. — With regard to the Avenarius, Thomson, and Tait expressions it may be remarked that they are not only mutually equivalent, but that if t_c or τ_c becomes 0° C. they reduce at once to the ordinary parabolic form of two terms:

$$\Sigma_0^t = at + bt^2.$$

They are all, therefore, forms which must apply if the latter purely empirical expression for the same temperature ranges applies, and with the same closeness, so that it is unnecessary to test more than

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one of the first four expressions against any one set of data. Also the fact that the Avenarius and Tait equations approximately conform to the observed data does not necessarily in any material degree strengthen the hypotheses which are adduced to show that these equations are a natural expression of the law.

Without attempting here a further analysis of the components making up the resultant emf. $\Sigma_c^h e$, which is the measured emf. of the thermo-couple, the proposed interpolation formulæ will be merely developed and applied. It may, however, be suggested in passing, that there seems to the writer to be little hope of arriving at a close approximation to the natural law except through an expression which shall contain separate terms representing the temperature function of the component arising at the contact of the dissimilar metals, and that arising from the inequality of temperature of the ends of each (homogeneous) element (Thomson emf.). The parabolic and Avenarius formulæ would comply in part with this requirement on the supposition that the emf. at contact varied as the first power, and the Thomson emf. in both wires as the square of the temperature. And looked at from that point of view, the neutral point would seem to have an explanation materially different from that usually accorded to it.

The Proposed Formulæ.

Exponential Equation. — The significance of this proposed expression may be thus stated. Suppose the cold junction of the couple be maintained at the absolute zero of temperature, $\tau = 0°$, and its emf. to be consequently zero. Let the other (hot) junction be at any temperature τ_h° absolute. The proposed equation is based on the assumption that the total emf. of the couple would then be representable by

$$e' = m\,\tau_h^n.$$

where m and n are numerical constants. If then the cold junction were raised to any temperature τ_c° there would be introduced an opposing emf. e'', which would be expressible by

$$e'' = m\,\tau_c^n.$$

The resultant emf. $\Sigma_c^h e$ would then be $e' - e''$, and therefore expressible by

$$\Sigma_c^h e = m\,\tau_h^n - m\,\tau_c^n. \qquad (6)$$

If in any instance, as is frequently the case in measurements, the temperature of the cold junction is maintained constant while that of the

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hot junction varies, then $m\,\tau_c^n$ becomes a constant, and it will be convenient to denote this constant by β when $\tau = 273°$ abs. $= 0°$ C. So that for this special case where the cold junction is at 0° C. and the hot junction at $t°$ C., we have

$$\Sigma_0^t e = m\,\tau^n - \beta. \tag{7}$$

This expression is not advanced as a possible natural form of the function $f(h,c)$. It is essentially empirical, and is not designed to account separately for the several distinct components entering into Σe. The fact that it closely fits the experimental data arises chiefly from the well known adaptability of the exponential equation to represent limited portions of curved lines. The equation also leads to certain inferences which appear inconsistent with the known thermo-electric laws, and fails to explain some known phenomena.

The evaluation of the constants m, n, and β is unfortunately attended by considerable labor. No application of the method of least squares readily presents itself, but by a method of successive approximations the values can be obtained with any desired degree of exactitude. Only two measured pairs of values of $\Sigma_0^t e$ and t are necessary for this approximation method, the third required pair being furnished by $\Sigma_0^0 e = 0$ and $t = 0$; although, of course, by the employment of three pairs of values well distributed in the data, a more closely fitting equation might frequently be obtained. The calibration of a thermo-couple for pyrometric work can thus be affected by the employment of but two known temperatures, and this, on account of the uncertainty of our knowledge of high melting points, is of great importance in high temperature work.

Let $t_0 = 0°$ C., t', and t'' be the selected observed temperatures from which to compute the constant, so that $\tau_0 = 273°$, $\tau' = t' + 273°$, $\tau'' = t'' + 273°$ abs. And let $\Sigma_0^{t_0} e = 0$, $\Sigma_0^{t'} e$, $\Sigma_0^{t''} e$, be the corresponding observed emfs. of the couple. Then, by substituting these in equation (7), and combining the three expressions, or their logarithms, we easily deduce

$$\beta = \frac{\Sigma_0^{t'} e}{\left(\frac{\tau'}{\tau_0}\right)^n - 1}; \tag{8}$$

$$n = \frac{\log\left(\Sigma_0^{t''} e + \beta\right) - \log\left(\Sigma_0^{t'} e + \beta\right)}{\log \tau'' - \log \tau'}; \tag{9}$$

$$m = \frac{\Sigma_0^{t''} e + \beta}{(\tau'')^n} \quad \text{or} \quad \frac{\Sigma_0^{t'} e + \beta}{(\tau')^n}. \tag{10}$$

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By means of these the numerical values of the constants may be calculated from those of τ', τ'', $\Sigma_0' e$, etc., as follows: —

1. Assume as a first approximation some value of n, say $n = 1$, unless some better approximation is in some way suggested. Substituting this value in (8), compute the corresponding value of β.

2. Using this as a first approximation, substitute it in (9) and compute the corresponding value of n.

3. Using this value as a second approximation to n, insert it in (8), and compute a second approximation to β.

4. With this compute a third approximation to n, and so continue until consistent values of β and n are found to the desired number of figures. Then compute m by (10).

The rate of convergence is not rapid, but after one or two approximations have been made an inspection of the rate will enable the computer to estimate values of n which will be nearer than the preceding approximation, and thus hasten the computation.

Where an equation is to be computed to best represent a progressive series of observed values of t and Σe, this method is of course open to some objections, since it incorporates in the constants the accidental errors of the selected observations from which the constants are deduced. This difficulty can be sufficiently overcome by computing residuals between the equation and the data, and amending the equation if necessary to give them a better distribution.

Logarithmic Formula. — A very simple expression for interpolation is of the general form

$$\Sigma_0' e = m t^n,$$

where m and n are constants. This serves fairly well for a short range, $t'' - t'$, when $t' - 0°$ is not less than one third of $t'' - t'$.

The convenience of the expression arises from two facts: first, that its two constants are very easily evaluated either by computation or graphically from the logarithmic expression (whence the name)

$$\log \Sigma_0' e = n \log t + \log m;$$

second, that its logarithmic plot is a straight line, since this expression is the equation to a straight line if we regard $\log \Sigma_0' e$ and $\log t$ as the variables. If, therefore, a series of values of Σe and t are known for a given couple, points obtained by plotting $\log t$ as abscissas and $\log \Sigma e$ as ordinates should lie along a straight line. Thus a couple may be completely "calibrated" for all temperatures by measuring Σe and t for any two values of t (suitably disposed). The constants m and n

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may be computed, or a plot of log Σe and log t may be made, and a straight line be drawn through them. Graphical interpolation on this line will then of course yield the values of log t and hence of t corresponding to observed values of Σe, and *vice versa*, and, if desired, the constants m and n. The expression for t as a function of Σe is, of course,

$$t = m' (\Sigma_0^t e)^{n'}, \quad \text{or} \quad t = \left(\frac{\Sigma_0^t e}{m}\right)^{\frac{1}{n}}.$$

This formula is well adapted to pyrometric work not of the very highest grade of accuracy, and has been advantageously employed in connection with the Le Chatelier thermo-electric pyrometer in a method to be described in a later article.

Test of Formulæ.

This will be made by applying the several formulæ to the experimental data of Barus, Holborn and Wien, Chassagny and Abraham, and Noll. These investigators employed modern methods of thermometry and of electrical measurement. Temperatures are either made in or reduced to the scale of the hydrogen (C. & A.), or of the air thermometer (B., H. & W., N.). Constants for the formulæ will be deduced, and the residuals or deviations of the data from the equations (i. e. δ = data-equation) will be computed for the observed points. For discussion these deviations will be expressed in percentages, viz. $100 \frac{\delta}{e}$, rather than in microvolts or degrees. This is preferable because the process of measurement of the emf., and to some extent at least of the temperature, is such as to yield results of a nearly constant fractional or percentage precision at all temperatures rather than of a constant number of microvolts or degrees. Thus by comparing percentages we eliminate a complication arising otherwise from the increasing value of δ as t increases. Incidentally there are also other well recognized advantages frequently attending the comparison of percentages rather than of absolute quantities.

The Barus Data. — Taking the data in the order of priority, those of Barus will be first employed. The measurements to be used consist of very elaborate and painstaking direct comparisons of several 20 per cent irido-platinum thermo-couples with several porcelain bulb air thermometers used under the constant pressure method.

Quotations of, or rather interpolations in, his original data* are

* Barus, C. U. S. Geol. Surv. Bull., No. 54 (1889). Phil. Mag., XXXIV. 1 (1892).

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given by Barus* later, as a basis from which to deduce constants for his proposed equation

$$e + e_0 = 10^{P+Qh} + 10^{P'+Q'c}.$$

Barus's numerical values for the constants are:

$e_0 = 45680$ microvolts.
$P = 4.6515$ " $Q = 1.106 \cdot 10^{-4}$.
$P' = 2.849$ " $Q' = 3.01 \cdot 10^{-3}$.

These constitute his "equation 3," for which e_0 corresponds to 20° C. The data and the deviations which I have computed for it, viz. δ = data-equation, are given in Table I. The last column gives the deviations expressed in percentages, viz. $100\frac{\delta}{E}$, where $E = e + e_0 + 1880$. This value of E is adopted to make the percentages comparable with those in subsequent discussions. The number 1880 is $1730 + 150$, which are the values of e_0 and $\Sigma_0^{20} e$ of the next two pages.

TABLE I.

BARUS'S AMERICAN JOURNAL OF SCIENCE DATA.

t^0	$e + e_0$ mv. Observed.	$e + e_0$ Computed from "Equ. 3."	δ mv.	$100\frac{\delta}{E}$ Per Cent.
° C.				
0	−150			
100	+680	653	+27	+1.11
200	1650	1657	−7	−0.20
300	2760	2788	−28	−0.60
400	3950	3994	−44	−0.80
600	6560	6551	+9	+0.11
800	9310	9273	+37	+0.34
1000	12200	12140	+60	+0.43

The lines AB and CD on the diagram (page 212), constructed with percentage deviations as ordinates and temperatures as abscissas show clearly that the deviations are systematic. Upon inspection of this plot

* Amer. Jour. Sci., XLVIII. 332 (1894). See also XLVII. 366 (1894).

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it appears that the data may be separated into two groups, one including 0°–300°; the other 400°–1000°, which appear to have entirely distinct forms of systematic error. This division corresponds to two distinct groups of data, one extending from 0° to 300°, the other including the second group and extending from 350° to 1075°. The latter were given in the Bulletin as the final results of the high temperature comparisons of the irido-platinum couple with porcelain bulb air thermometers. The detailed statement of the 0°–300° comparison I have not seen. Although the discrepancy between the two sets of systematic deviations is not extremely large, yet it has seemed to me that it was beyond the limits of concordance in the higher temperature work, and that it would be better for the present purpose to deal solely with the 350°–1075° data. Two points regarding Barus's work should be noticed: one the strikingly high degree of concordance between individual observations even with different thermometer bulbs and different thermo-couples; the other the remark in which Barus notes a possibility of being able still further to reduce the "stem error" entering into the result, which so far as I am aware has not yet been done.

The high temperature air thermometer comparisons (Bulletin, Series I., II., III., IV., and V.) of Barus are so numerous (108) and so distributed that the labor of utilizing them simply for deducing constants and testing an equation would be excessive. Also they are too concordant to permit interpolation on a direct plot without a sacrifice of some of their precision. For the purposes of discussion, therefore, I averaged them in nine groups. The first group contained all where the emf. lay between 3,000 and 4,000 microvolts; the second group between 4,000 and 5,000 mv.; and so on by steps of 1,000 microvolts, except that the seventh group covered 2,000 mv. from 9,000 to 11,000. These groups were not exactly equal in number of observations, and therefore in weight, nor is the arithmetical average a strictly legitimate value where the function is not linear; but, as easily seen by inspection of the originals, the errors thus introduced are negligible. In Table II., columns one and two give the direct values of the averages. Column three reduces $\Sigma^t_{20} e$ to $\Sigma^t_0 e$ by adding 150 microvolts the value of $\Sigma^0_{20} e$ being elsewhere given by Barus as —150 microvolts.

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TABLE II.

BARUS'S AIR THERMOMETER COMPARISONS, SERIES I.–V.

t^0	$\Sigma_{20}^{t} e$	$\Sigma_{0}^{t} e$	Avenarius.		Exponential.		Logarithmic.	
			δ Data Eq.	Per Cent $= 100\frac{\delta}{e}$	δ Data Eq.	Per Cent $= 100\frac{\delta}{e}$	δ Data Eq.	Per Cent $= 100\frac{\delta}{e}$
° C.	mv.	mv.	mv.		mv.		mv.	
0.0	(−150)	0	0	0.0	+23	+1.3		
378.5	3679	3829	−84	−4.0	−66	−1.2	−33	−0.60
440.3	4508	4658	+18	+0.28	+18	+0.28	+30	+0.47
522.0	5486	5636	−4	−0.07	−25	−0.34	−36	−0.50
588.4	6404	6554	+70	+1.1	+33	+0.40	+9	+0.12
672.1	7550	7700	+110	+1.5	+60	+0.64	+26	+0.28
745.6	8530	8680	+82	+0.92	+26	+0.25	−9	−0.10
840.1	9898	10048	+101	+1.0	+49	+0.41	+26	+0.22
946.6	11396	11546	+9	+0.07	−19	−0.14	−13	−0.10
1019.7	12475	12625	−45	−0.32	−45	−0.32	−10	−0.07
Average percentage deviations . .			0.93			0.53		

The Avenarius equation applied to these data yields

$$\Sigma_0^t e = 9.104\, t + 3.249 \cdot 10^{-3} t^2.$$

Microvolts. Range 350° to 1075° C.

Computing from this equation values of $\Sigma_0^t e$ for the successive values of t in column one, and subtracting them from the data in column three gives the deviations between data and equation. These are expressed in microvolts in column four, and in percentages in column five, the percentage being reckoned in terms of e_t as deduced by the exponential formula. Objections may be felt to this use of e_0 (here as throughout the subsequent tables) as a basis, since e_t involves e_0, which is an extrapolated value, certainly not exact, and possibly wide of the truth. Such a criticism is valid, but inasmuch as the values of e_0 employed are nearly equal, and as the percentage deviations are used merely for purposes of expressing relative accuracy, the possible

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error involved is nearly annulled. Hence, although it would be better to compute δt, and express this as a percentage of the absolute temperature τ, the added labor did not seem justified by the small gain.

The exponential equation applied to the Barus data yields

$$\Sigma_0' e = 0.7691\ \tau^{1.373} - 1730, \text{ or}$$

$$e_\tau = 0.7691\ \tau^{1.373}, \text{ and } \beta = 1730 \text{ mv.}$$

Range of data 350° to 1075° C.

[N.B. This equation was deduced with the value 0°C. = 273°.7 absolute, whereas in all subsequent tables 0°C. = 273°.0 absolute is employed as a more probable value. The numerical values of the constants are therefore subject to a slight modification, but as for the present purpose we are concerned only with δ, which would not be sensibly changed, the recomputation is not worth while.]

Columns six and seven, Table II., give δ and its percentage value for the exponential equation.

The Barus Equation. — The excessive labor involved in the evaluation of the constants P, Q, P', and Q' of Barus's proposed equation detracts so seriously from its usefulness that I have also allowed it to deter me from computing them for the above tabulated values. The comparison of the values of δ for his "Equation 3," and for an approximate exponential of my own based on the same data, is, however, decidedly in favor of the latter.

The logarithmic equation applied to the Barus data yields

$$\Sigma_0' e = 2.665\ t^{1.220},$$

or its equivalent,

$$\log \Sigma_0' e = 1.220 \log t + 0.42570.$$

The deviations are given in the last two columns of Table II.

Holborn and Wien Data. — This important comparison * of the rhodo-platinum thermo-couple with the porcelain bulb air thermometer up to high temperatures was performed under the auspices of the Reichsanstalt at Berlin, and appears to be on the whole the most important and reliable contribution to this subject in recent years. The experimental work was evidently conducted with great care, and although not showing the concordance of results, nor the multiplication of observations of Barus's work, yet in respect to stem-exposure correction, to exposure of the thermal junction, and to direct measurement of the coefficient of expansion of the bulb, it is probably more

* Holborn and Wien. Zeit. f. Instk., XII. 257, 296 (1892). Also in full in Wied. Ann., XLVII. 107 (1892).

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free from systematic error. It is to be regretted that the results were not more thoroughly discussed, and that neither a chemical analysis nor even a statement was given to indicate the reliability of the stated percentage composition of the various alloys used. For when closely examined, the data seem to indicate a definite relation between the composition and the emf., as was shown by a relation discovered between the constants in my exponential equations for the various alloys. The deviations were only such as might be attributed to uncertainty of composition, but as no measure of the latter was given, a statement of the relations and interesting inferences from them is not warranted. It is also unfortunate that an analysis, or at least a definite statement of the percentage purity, was not given for the gold, copper, and silver whose melting points were observed. The assertion that the gold showed on qualitative analysis only a trace ("Spur") of copper, and the silver a "trace" of iron, is hardly definite. The value of the whole work would have been enhanced by these additions far more than in proportion to the comparatively small labor demanded by them, and such completeness is naturally to be expected in work emanating from this source. It is to be hoped that a continuation of this research is in progress, and that additional high melting points may be measured.

Table III., columns one and two, quotes the interpolated mean values of several comparisons expressed in international microvolts and degrees centigrade. With regard to these data it should be stated that below about 400° they were not supposed to be of as high accuracy as above that point. Also, that, owing to unavoidable circumstances, the data below 300° were obtained with only a single air thermometer bulb, and similarly those above about 1300° with one bulb only, but a different one, while the data intermediate between 400° and 1300° are the mean of observations with the two bulbs. This fact may partially account for the erratic character of the residuals above 1300°, where the deviations are so great and so distributed (see diagram, page 212) as to render these observations of very little service. Direct comparison with the air thermometer was made with one 10 per cent rhodo-platinum couple "A" only.

The parabolic formula applied to these by Holborn and Wien, when corrected as to decimal points,* is

* The equation at both references, and stated to be in microvolts and degrees, is erroneously printed as

$$\text{“}t = f(e) = 13.76\,e - 0.004841\,e^2 + 0.000001378\,e^3.\text{”}$$

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$$t = 1.376{\cdot}10^{-1}\,(\Sigma_0^t e) - 4.841{\cdot}10^{-6}\,(\Sigma_0^t e)^2 + 1.378{\cdot}10^{-10}(\Sigma_0^t e)^3.$$

Range −80° C. to +1445° C.

The residuals are given in Table III., columns three and four.

TABLE III.

HOLBORN AND WIEN. AIR THERMOMETER COMPARISONS, ALLOY A.

t Centigr.	$\Sigma_0^t e$ mv.	H. and W. Eq. δ = Data − Eq. mv.	H. and W. Eq. Per Cent $= 100\frac{\delta}{e}$	Avenarius. δ = Data − Eq. mv.	Avenarius. Per Cent $= 100\frac{\delta}{e}$	Exponential. δ = Data − Eq. mv.	Exponential. Per Cent $= 100\frac{\delta}{e}$	Logarithmic. δ = Data − Eq. mv.	Logarithmic. Per Cent $= 100\frac{\delta}{e}$
° −80	−361	—		—		—		—	
0	0	0	0	0	0	0	0	0	0
+82	+500	−84	−4.6	−107	−5.1	−69	−3.6	+40	+2.20
154	1000	−147	−6.1	−166	−7.2	−122	−4.8	+11	+0.50
220	1500	−135	−5.0	−199	−7.1	−140	−4.7	−27	−1.00
273	2000	−150	−4.5	−142	−4.3	−85	−2.6	+16	+0.50
329	2500	−130	−3.6	−124	−3.3	−73	−1.9	+11	+0.30
379	3000	−60	−1.4	−66	−1.5	−24	−0.57	+45	+1.00
431	3500	−30	−0 60	−41	−0.90	−6	−0.12	+45	+0.90
482	4000	0	0.00	−14	−0.22	+8	+0.15	+41	+0.80
533	4500	+10	+0.17	−1	0	+9	+0.15	+27	+0.50
584	5000	0	0.00	0	0	−2	−0.03	+1	+0.01
633	5500	0	0.00	+9	+0.13	−4	−0.06	−13	−0.20
680	6000	+10	+0 11	+28	+0.38	+5	+0.07	−15	−0.20
725	6500	+30	+0.40	+58	+0.74	+26	+0.33	−1	−0.01
774	7000	−10	−0.12	+35	+0.42	−5	−0.06	−39	−0.47
816	7500	+20	+0.22	+78	+0.90	+33	+0 37	−8	−0.10
862	8000	0	0.00	+69	+0.74	+19	+0 20	−24	−0.26
906	8500	−20	−0.20	+72	+0.74	+19	+0.20	−25	−0.25
952	9000	−55	−0.55	+44	+0.43	−.10	−0.10	−53	−0.52
996	9500	−88	−0.80	+29	+0.26	−24	−0.22	−67	−0.60
1038	10000	−88	−0.80	+29	+0.25	−20	−0.18	−57	−0.50
1080	10500	−100	−0.85	+22	+0.20	−23	−0.20	−54	−0.43
1120	11000	−100	−0.80	+31	+0.25	−7	−0.06	−22	−0.19
1163	11500	−140	−1.10	−6	−0.05	−33	−0.26	−51	−0.40
1200	12000	−96	−0.74	+26	+0.20	+9	+0.07	+2	+0.02
1241	12500	−96	−0.70	0	0	−3	−0.03	−8	−0.06
1273	13000	0	0.00	+84	+0.60	+94	+0.67	+111	+0.80
1311	13500	+36	+0.24	+84	+0.57	+110	+0.80	+140	+0.90
1354	14000	+24	−0.17	+10	+0.07	+.58	+0.38	+107	+0.70
1402	14500	−60	−0.40	−141	−0.90	−65	−0.41	+2	+0.01
1445	15000	−72	−0.45	−231	−1.40	−128	−0.80	−38	−0.23
ad. for 0 to 1445.			1.12		1.15		0.77		1.46
ad. for 431 to 1445.			0.39		0.43		0.25		0.38
ad. for 431 to 1241.			0.43		0.36		0.15		0.34

The Avenarius Formula applied to the Holborn and Wien data with constants deduced from $t = 584°$ and $1273°$ becomes

$$\Sigma_0^t e = (t - t_0)\,\{7.2188 + 0.00\,229\,94\,(t + t_0)\}, \text{ or}$$
$$= 7.2188\,t + 2.2994{\cdot}10^{-3}\,t^2.$$

Range 0° to 1445° C.

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The deviations in microvolts and percentages from this equation are given in columns five and six, Table III.

The exponential equation fitting these data most closely, and coinciding with them as nearly the same points as the others, viz., at about 584° and 1250°, is

$$\Sigma_0^t e = 0.57\,674\ \tau^{1.377} - 1310, \text{ or}$$
$$e = 0.57\,674\ \tau^{1.377}, \beta = 1310.$$
$$\text{Range } 0° \text{ to } 1445° \text{ C.}$$

The deviations in microvolts and percentages are in columns seven and eight, Table III.

The logarithmic equation applied to the Holborn and Wien data on A yields

$$\Sigma_0^t e = 2.1682\ t^{1.2156}, \text{ or}$$
$$\log \Sigma_0^t e = 1.2156 \log t + 0.36\,610.$$

The deviations are given in the last two columns of Table III.

Holborn and Wien not only compared the ten per cent rhodo-platinum couple A directly with the air thermometer, but compared with A seven other couples in which one element was platinum, and the other a rhodo-platinum alloy, the percentage of rhodinum being stated respectively as, for C_1 and C_2, 10 per cent (these two I have combined under C), D, 9 per cent, E, 11 per cent, F, 20 per cent, G, 30 per cent, H, 40 per cent. For the present purpose I have combined these data, which were differences of emf. between C and A, D

TABLE IV.

Designation of the Alloy.	Nominal Percentage of Rhodium.	Expon. Eq. Constants.		
		m	n	$\frac{\beta}{mv.}$
D	9	1.36 71	1.250	1517
C	10	0.95 596	1.310	1485
E	11	0.81 734	1.336	1469
A	10	0.57 689	1.377	1305
F	20	0.22 865	1.522	1167
G	30	0 06 599 0	1.708	956
H	40	0.06 303 4	1.720	977

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and A, etc., with the corresponding emf. of A, and thence have deduced the exponential equations for each of the alloys. Table V. gives the percentage deviations of these alloys from the exponential equation (data — equation), and Table IV. shows the values of m, n, and β for those equations.

TABLE V.

HOLBORN AND WIEN. — COMPARISON OF ALLOYS.

t	D	A	C	E	F	G	H	Average.
°C. 154	—	−4.8	—	−4.0	—	−5.0	−4.4	−4.5
273	−0.9	−2.6	−2.7	−2.2	−2.3	−3.5	−2.3	−2.6
379	+2.1	−0.57	−0.80	−0.50	−1.3	−0.60	−0.25	−0.67
482	+2.6	+0.15	−0.03	0.	−0.60	+0.22	+0 46	−0.03
584	+0.9	−0.03	+0.19	+0.08	+0.13	+0.30	−0.03	+0.02
680	−0.30	+0.07	+0.13	+0.13	+0.12	−0.16	−0 26	0.
774	−0.19	−0.06	−0.08	−0.02	−0.12	−0.42	−0.46	−0.19
862	+0.23	+0.20	+0.20	+0.20	+0.09	+0.15	−0.11	+0.12
952	+0.20	−0.10	0.	−0.11	−0.15	+0.09	−0.24	−0.08
1038	+0.12	−0.18	−0.10	−0.21	−0.27	+0.04	−0.14	−0.16
1120	−0.15	−0.06	−0.09	−0.02	+0.10	−0 01	+0.22	−0.01
1200	+0.02	+0.07	0.	+0.10	0.	+0.04	0.	+0.03
1273	—	+0.67	+0.70	+0.80	+0.80	−0.43	+1.00	+0.73
1354	—	+0.38	+0.60	+0.67	+0.51	+0.30	+1.00	+0.58
1445	—	−0 80	−0.38	−0.50	—	−0.90	−0.40	−0.60
a. d. 400–1200	0.52	0.15	0.09	0.10	0.12	0 16	0.21	0.07
a. d. 400–1445	—	0.25 Direct from Air Th.	0.21	0.24	(0.24)	0.23	0.36	

*Chassagny and Abraham Data.** — The apparently very careful measurements of these observers cover a range of 0° to 100° C. with

* Chassagny et Abraham. Ann. de Chim. et de Phys., XXVII. 355 (1892).

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observations at 25°, 50°, and 75° only. The range is too short, and the intervals are too great to render the work of much service in testing a general formula, but if its accuracy is as high as about 0°.01, as it appears to be, this in part offsets the disadvantage. Measurements of $\Sigma_0' e$ and t were made with four thermo-couples with the results shown in Table VI. (international microvolts and degrees centigrade on hydrogen scale).

TABLE VI.

Couple.	$\Sigma_0^{100} e$	$\Sigma_0^{75} e$	$\Sigma_0^{50} e$	$\Sigma_0^{25} e$
Fe–Cu	1093.2	864.9	604.8	315 5
Fe–Pt Rh	895.1	708.9	496.1	259.1
Fe–Ag	1123.0	885.6	617.4	321.1
Fe–Pt	1685.1	1278.9	859.9	432.1

The Avenarius equation was applied to these data by Chassagny and Abraham in the form

$$\Sigma_0' e = a\,t + b\,t^2.$$

They evaluated the constants from the 50° and 100° data. With these they computed the temperatures which the equation would yield by insertion of the observed values $\Sigma_0^{25} e$ and $\Sigma_0^{75} e$. These values are given in Table VII., columns two and three.

The exponential equation applied to these data for Fe – Pt becomes

$$\Sigma_0' e = 105.096\ t^{0.7360} - 6525.3 \quad [\text{Range } 0° \text{ to } 100° \text{ C.}].$$

The values of t corresponding to the observed values $\Sigma_0^{25} e$ and $\Sigma_0^{75} e$ are given in Table VII. It has not seemed for the present purpose worth while to make similar computations for the other couples, as they would not materially affect the inferences to be drawn.

The logarithmic equation yields

$$\Sigma_0' e = 19.2946\ t^{0.970535};$$
$$\log \Sigma_0' e = 0.97\ 059\ 5 \log t + 1.28\ 543\ 6.$$

The deviations are given in the table.

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TABLE VII.

Couple.	Avenarius.		Exponential.				Logarithmic	
	t	δt	t	δt	δ mv.	$100\,\delta/e$ Per Cent.	δt	δ mv.
Fe–Cu	24.88°	+0.12°	°	°			°	
Fe–Pt Rh	24.885	0.115						
Fe–Ag	24 87	0.13						
Fe–Pt	24.87	0.13	24.80	+0.20	−2.6	−0.037	+0.52	−6.7
Fe–Cu	75.13	−0.13						
Fe–Pt Rh	75.135	0.135						
Fe–Ag	75.135	0 135						
Fe–Pt	75.135	0.135	75.15	−0.15	+2.5	+0.032	−0.26	+4.3

The Noll Data. — A contribution of much permanent value to the data on thermo-electrics has recently been made by Noll,* who has measured $\Sigma_0^t e$ and t for thirty-two couples over a range in most cases of 0° C. to 218° C. The metals employed (including carbon) were usually of a high and stated degree of purity, and consisted of eighteen different substances, two of which were alloys (German silver and brass), and the remainder samples of different degrees of purity or hardness of the pure substances. The couples contained, as one element, for the most part, either copper or mercury. Temperatures were reduced to the air thermometer scale.

The Avenarius formula was applied to fourteen of the more important of them by Noll. The deviations are given in Table VIII.

The exponential equation I have applied to the same data. It has not seemed essential to reproduce here the entire series of data, and the deviations of both equations. They are, therefore, presented in a somewhat more digested form. Table VIII. gives the constants for the exponential equation (those for the Avenarius may be found in Noll's article), the mean deviations (= data − equation) for each series, and the mean percentage deviations (= 100 δ/e). (See remark as to use of e under "Barus Data.") Table IX. groups the percentage deviations under their nearest values of t for exhibiting their systematic

* Noll, Wied. Ann., LIII. 874 (1894).

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character. The fact that the experimental method brought the observations all very nearly to the respective temperatures t given in the table renders this grouping possible. I have taken the liberty of correcting a few obvious numerical errors, and of dropping a very few values evidently containing a mistake.

TABLE VIII.

NOLL'S DATA ON PURE METALS.

Couple.	m	n	β mv.	Av. Pct. Deviation.	
				Avenarius.	Expon.
Au–Hg	$4.6954 \cdot 10^{-3}$	2.136	750.4	±0.27	±0.17
Ag–Hg	$2.8637 \cdot 10^{-3}$	2.206	677.8	0.33	0.15
Ni–Cu	$8.2333 \cdot 10^{-1}$	1.511	3950.2	0.30	0.17
(Cd–Cu	$3.7617 \cdot 10^{-11}$	4.94	40.7	0.48	3.40)
Br–Cu	$2.4969 \cdot 10^{-1}$	1.566	531.1	0.14	0.13
Zn–Hg	$8.2890 \cdot 10^{-4}$	2.420	651.6	0.15	0.18
Pb–Cu	$1.7674 \cdot 10^{-2}$	1.800	429.0	0.05	0.07
Cu_1–Hg	$4.6726 \cdot 10^{-3}$	2.130	768.4	0.12	0.11
[Fe–Hg	$1.0913 \cdot 10^{+2}$	0.7220	6264.2]		
Co–Hg	$8.3295 \cdot 10^{-3}$	2.166	1575.2	0.26	0.22
Pt_1–Cu	$2.1475 \cdot 10^{-3}$	2.266	711.1	0.08	0.12
Pt_2–Cu	$1.1095 \cdot 10^{-3}$	2.353	599.0	0.19	0.25
Sn_1–Cu	$4.2021 \cdot 10^{-2}$	1.667	482.8	0.21	0.09
Mg–Cu	$2.0449 \cdot 10^{-2}$	1.782	448.7	0.15	0.17
Al–Cu	$7.5643 \cdot 10^{-2}$	1.590	565.3	0 11	0.12
G. s.–Cu	$2.0454 \cdot 10^{-1}$	1.684	2589.9	0.06	0.05
Average omitting Cd–Cu and Fe–Hg				±0.17	±0.14

It may, perhaps, not be out of place here to caution those who would make use of Noll's data to their full accuracy that his original, and not his interpolated, numbers should be resorted to. The approxi-

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mate linear interpolation which he has employed is not as accurate as his experimental data demand.

The logarithmic equation applied to the Cu–Hg couple as typical of the Noll data yields

$$\Sigma_0' e = 2.57\,434\ t^{1.2250};$$

or

$$\log \Sigma_0' e = 1.2250 \log t + 0.41\,066\,5.$$

The residuals to this expression are given in Table IX.

TABLE IX.

AVENARIUS EQUATION. — DATA MINUS EQUATION IN PER CENT.

	15°	57°	100°	138°	181°	198°	217°
Au–Hg	−0.10	−0.40	0	+0.05	+0.60	+0.90	0.
Ag–Hg	−0.13	+0.20	0	+0.21	−0.50	−1.30	0.
Ni–Cu	−0.26	−0.15	0	0.	−0.22	−0.31	−1.17
Br–Cu	—	−0.10	0	+0.20	+0.17	+0.35	0.
Zn–Hg	—	−0.03	0	+0.09	+0.41	+0.40	0.
Pb–Cu	—	−0.03	0	−0.11	+0.12	−0.04	0.
Cu_1–Hg	+0.02	−0.16	0	+0.01	+0.15	+0.38	0.
Co–Hg	—	—	0	+0.42	0.	—	−0.56
Pt_1–Cu	—	−0.12	0	−0.06	+0.09	+0.21	0.
Pt_2–Cu	—	−0.13	0	−0.11	0.	+0.67	−0.21
Sn_1–Cu	—	−0.20	0	0.	+0.34	+0.40	+0.30
Mg–Cu	—	+0.11	0	+0.22	−0.37	+0.11	0.
Al–Cu	—	+0.16	0	+0.18	−0.18	+0.15	0.
G. s.–Cu	—	−0.01	0	+0.16	+0.11	—	0.
Average	−0.12	−0.07	0	+0.09	+0.05	+0.16	−0.12

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TABLE IX. — *Continued.*

EXPONENTIAL EQUATION. — DATA MINUS EQUATION IN PER CENT.

	15°	57°	100°	138°	181°	198°	217°
Au-Hg	+0.01	−0.12	−0.06	−0.06	+0.09	+0.12	−0.80
Ag-Hg	−0.18	+0.22	0.	+0.05	−0.03	0.	−0.50
Ni-Cu	−0.26	−0.16	0.	+0.07	0.00	0.	−0.72
Br-Cu	—	−0.06	−0.01	+0.12	+0.20	−0.26	−0.13
Zn-Hg	—	−0.30	+0.02	+0.14	+0.10	+0.65	−0.04
Pb-Cu	—	−0.10	0.	−0.25	+0.04	0.	0.00
Cu_1-Hg	−0.19	−0.27	+0.01	—	−0.03	0.	−0.25
Co-Hg	—	−0.05	+0.01	+0 48	−0.01	—	−1.00
Pt_1-Cu	—	−0.15	+0.03	−0.06	+0.17	0.	−0.31
Pt_2-Cu	—	−0.56	0.	−0.10	−0.16	+0.70	0.
Sn_1-Cu	—	−0.04	+0.04	−0.29	+0.12	+0.06	0.
Mg-Cu	—	+0.18	0.	+0.15	−0.52	+0.17	0.
Al-Cu	—	+0.16	0.	+0.12	−0.24	+0.18	0.
G. s.-Cu	—	+0.07	−0.01	+0.08	—	—	+0.05
Average	−0.16	+0.08	+0.01	+0.03	−0.02	+0.14	−0.27

LOGARITHMIC EQUATION. — DATA MINUS EQUATION IN PER CENT.

Cu_1-Hg	+2.3	+1.5	0.	−0.40	0.	+0.50	+0.80

DISCUSSION OF THE DEVIATIONS.

Plots are given in the following diagram with temperatures as abscissas and percentage deviations between the data and the sundry equations as ordinates, i. e. $100\ \delta/e$ where δ = data-equation. Inspection will show that with one exception (viz. the logarithmic equation applied to the Barus data) these plots, whether the equation is the ordinary parabolic, the Avenarius, the Barus, the exponential, or the logarithmic, have the same general form, which may be imperfectly

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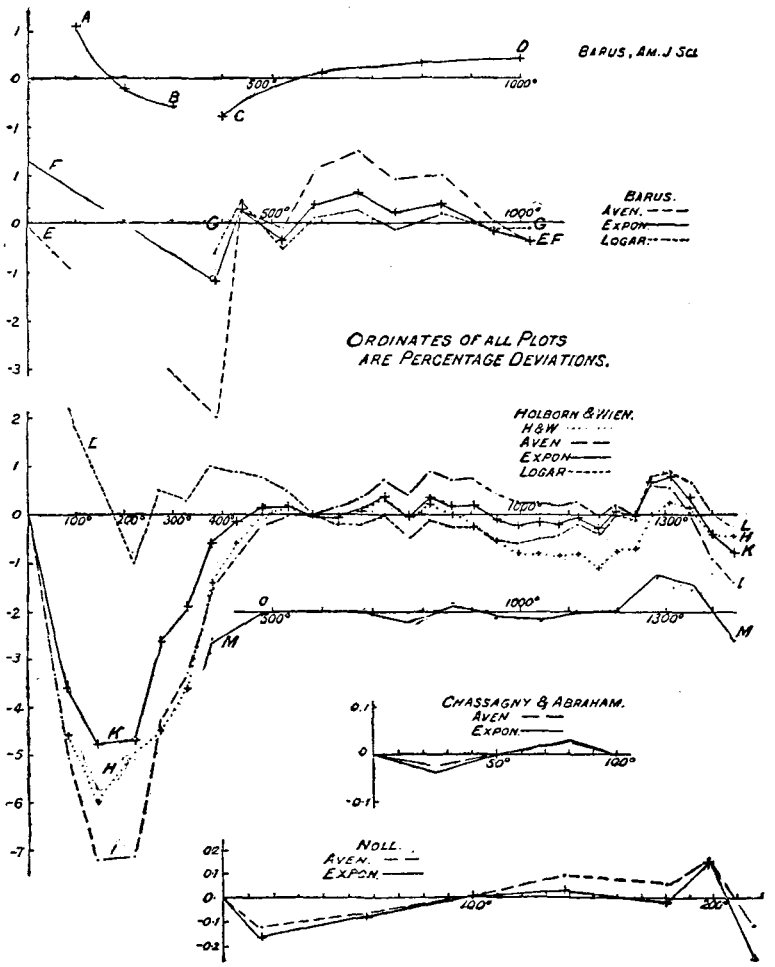
dsecribed as follows. If the equation be made to conform to the data at 0°C. and at two higher points, a and b, then the deviation will be of the negative sign from 0 to a, positive from a to b, and negative above b.



The slight departures from this general form are clearly due either to accidental errors, or to failure to make the equation conform to the data at all three points, or at suitable ones. The evidence is therefore conclusive that *for all of the expressions the deviations are systematic and not purely "accidental" in character.*

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One of two inferences is therefore warranted: —

1. *That neither the parabolic, Avenarius, Barus, exponential, nor logarithmic equation is the natural expression of the function.*

2. Or that the scale of temperature to which the values of t are referred in the foregoing investigations departs from the normal scale by an amount and system roughly indicated by the above residual plots.

The latter inference, suggested by Chassagny and Abraham in the interpretation of their results, does not seem to possess much weight, notwithstanding the urgent need of renewed elaborate experimental investigation of the relation between the hydrogen, air, and thermodynamic scales of temperature.

As to the relative usefulness of the various expressions for purposes of interpolation and extrapolation some further inspection is necessary. The Barus equation 3, line *CD*, shows slightly smaller deviations on the plot than do the Avenarius and exponential, lines *EE* and *FF*. This, however, is due to the fact that the data against which 3 is tested are mean interpolated values, and hence have a sensibly less variable error than those against which the other equations are tested. An approximate exponential equation showed less deviations than 3 against the same data. There seems, therefore, to be no advantage in this equation sufficient to offset the difficulty of evaluation of its constants.

Applied to the Barus data from 350° to 1250°, the exponential equation shows deviations considerably less than one half as great as those of the Avenarius, while those of the logarithmic equation are so small as to lie far within the range of the variable errors, and they moreover show no clear evidence of systematic error between these limits of temperature. *For interpolation in the Barus data, therefore, the logarithmic equation is far preferable*, and must be conceded to be representative of the data. *For extrapolation* it is undoubtedly better than the Avenarius, which (as would the exponential in less degree) would certainly give above 1000° extrapolated values of Σe too large, or of t too small. The advantage due to its simplicity is also to be noted.

Applied to the Holborn and Wien data from 400° to 1450° the exponential equation shows (line *KK*) the same sort of superiority to both logarithmic (line *LL*) and Avenarius (line *II*) that the logarithmic shows to the others with the Barus data, but in a still more marked degree. Within the limits 450° to 1450°, in fact, the distribution of the residuals to the exponential is such as not to warrant

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of itself alone any inference of systematic departure, especially when the mean line *MM* from all the couples is considered. It will be noted as an important confirmation of both the exactness of the electrical measurements in the investigation and the applicability of the exponential formula through a considerable range of alloys (and therefore of values of m and n) that this mean line *MM* is almost identical in form with the line *KK* for alloy A. Relatively to the Holborn and Wien formula (line *HH*), the exponential possesses a similar advantage, with also the merit of greater simplicity of form.

It may therefore be affirmed that *for interpolation between* 450° *and* 1450° *in the H. and W. data the exponential equation is abundantly exact. For extrapolation* above 1450° it would not be entirely safe, although presumably better than the others, since the departure between 0° and 450°, and the similarity of the form to others, makes a systematic departure sufficiently certain.

Applied to the Chassagny and Abraham data, 0°–100°, and to the Noll data, 0°–218°, (see diagram.) the Avenarius and exponential formulæ show about equal deviations, but with the advantage slightly on the side of the former. In the case of the Noll data, the line indicates that the systematic error is slightly greater for the exponential than for the Avenarius expression. The average deviations in Table IX., on the contrary, show that for each individual equation the concordance is greater for the exponential than the Avenarius. This discrepancy is due to the fact that, in order to eliminate local accidental errors, the equations (both Avenarius and exponential) are not all made to coincide with the data at the same temperatures, so that the process of averaging by which the data for the Noll plots is obtained is not numerically rigid. This does not, however, sensibly affect the general form of the curve. The greater ease of computation of the numerical constants of the Avenarius expression, and its applicability where both t and t_0 change, ought not to be overlooked. For extrapolation the exponential would be safer, for the reason that it has been above shown that for long ranges its systematic error is less.

The logarithmic equation fits the Noll data very badly, as shown by the deviation in Table IX. (not plotted), and also is much less close to the Chassagny and Abraham data than are the others.

THE GENERAL CONCLUSION as to applicability, then, seems to be that, while the *Avenarius* expression may be equally good or better than the exponential *for interpolation over short ranges*, yet *for inter-*

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polation over long ranges and for extrapolation above the observation limits the exponential is decidedly preferable. The exponential form is also preferable to the remaining expressions with the exception noted.

The logarithmic form, although closely applicable to the Barus data, is of more doubtful general value, yet on account of its great convenience it may find application in industrial pyrometry, as will be elsewhere indicated. Although failing below 300° or 400°, it may probably be applied to the irido- or rhodo-platinum couple between 400° and 1200° C. with a maximum error not exceeding about 5°. If extended to cover 400° to 2000° the error might rise to 15° or 20°.

More in detail it may be briefly noted by way of summary : —

That the logarithmic equation fits the Barus data between 400° and 1250° with scarcely sensible systematic error, and within the limits of variable errors of the data.

That the exponential equation similarly fits the Holborn and Wien data within the limits 400° to 1445°.

That when made to coincide with the data at about 450° and 1200° the systematic deviations of the exponential equation from the Barus data, and of the logarithmic equation from the Holborn and Wien data, are in general of opposite sign and of roughly equal magnitude.

Barus Melting and Boiling Point Data.

From the foregoing demonstration of its applicability, it seems proper to apply the logarithmic formula to the Barus thermo-electric data on melting points.*

Whether the extrapolation above 1000° by the logarithmic formula is entitled to any great weight may be questioned, but there is no obvious reason why it is not more reliable than by any of the others. I have employed the equation given on page 202, which represents very closely Barus's high temperature air thermometer comparisons, calculating thence the temperatures t corresponding to the values of $\Sigma_{20}^{t} e$ given by Barus for the various points, assuming Barus's value $\Sigma_{0}^{26} e = 150$ mv. The results are given in column three of Table X. Column four quotes the most reliable previous determinations of the same points by other observers. As to which of the two columns of results best represents Barus's work there can be little doubt from the above evidence that below 1000° it is the second, that

* Amer. Jour. Sci., XLVIII. 332 (1894).

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is, the one computed from the logarithmic equation. These combine both his own air thermometer and melting point work. Above 1000° the logarithmic values are probably slightly too high.

TABLE X.

BARUS MELTING AND BOILING POINTS.

	Computed by Eq. 3.	Computed by Log. Eq.	Data by other Observers.	
Mercury (B. Pt.)	357°	359°	356.76°	Callendar and Griffiths.
Zinc	420	423	417.57	" "
Sulphur (B. Pt.) .	446	449	444.53	" "
Aluminum . . .	638	641	635	Le Chatelier.
Selenium (B. Pt.)	694	697		
Cadmium (B. Pt.)	782	782		
Zinc (B. Pt.) . .	929	926	930	Deville and Troost.
Silver	986	985	968	Holborn and Wien.
			954	Violle.
Gold	1091	1090	1072	Holborn and Wien.
			1035	Violle.
Copper	1096	1095	1082	Holborn and Wien.
			1054	Violle.
Bismuth . . .	1435	1441		
Nickel	1476	1485	1450	Carnelly and Williams.
Palladium . . .	1585	1597	1500	Violle.
Platinum . . .	1757	1783	1775	Violle.

REMARK.

Review of the laborious researches which have been devoted to the direct comparison of thermo-electric elements with the air thermometer, mainly for the purpose of advancing the art of pyrometry, has enforced the conviction that, at least for the immediate future, this end would be better served by accurate gas thermometer meas-

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urements of melting points of metals. Each such determination made upon a reproducible metal of known high purity under proper reproducible conditions fixes an enduring and reproducible reference point, a pyrometric "bench mark." And there are enough inexpensive metals, together with a possible system of simple alloys, to give points of sufficient frequency. These would then afford a convenient means of obtaining accurately known high temperatures for purposes of study of all high temperature phenomena, and particularly for calibrating thermo-electric, electrical resistance, optical, or other secondary pyrometric interpolation apparatus, — for it must be remembered that all such apparatus is necessarily secondary, the gas thermometer being inevitably the primary.

On the other hand, comparison with the air thermometer of a thermo-couple, or of a resistance pyrometer, or the study of any progressive thermal phenomenon, while it possibly may result in the eduction of a natural law, is very unlikely to lead to anything more than the establishment of an approximate equation with constants characteristic only of the individual materials actually employed, and not transferable to other, although similar materials. Such results are obviously of a much more ephemeral character than the melting point measurements. Even when any pyrometer thus tested is applied to the establishment of melting points, it must at best yield results inferior to direct application of the gas thermometer, except in cases where the latter is hampered by want of sufficient quantity of the metal to be experimented upon, — a condition which need only affect such costly substances as gold and platinum.

Stated broadly, the great need of the art of pyrometry is convenient methods of producing, or of recognizing when produced, a series of accurately known high temperatures. The analogous problem has been partially solved for thermometry at temperatures up to 300° C. by the investigation of boiling points of certain chemically pure substances under controlled pressures.

Rogers Laboratory of Physics,
Massachusetts Institute of Technology,
Boston, September, 1895.

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INVESTIGATIONS ON LIGHT AND HEAT, MADE AND PUBLISHED WHOLLY OR IN PART WITH APPROPRIATION FROM THE RUMFORD FUND.

XI.

CONTRIBUTIONS FROM THE PHYSICAL LABORATORY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.

XLV. — MELTING POINTS OF ALUMINUM, SILVER, GOLD, COPPER, AND PLATINUM.

BY S. W. HOLMAN, WITH R. R. LAWRENCE AND L. BARR.

Presented November 13, 1895.

THE following melting points are offered as provisional only, but with the belief that they are more reliable than previous data. The absolute values depend in part upon the assumption of 1072° C. as the melting point of pure gold, the recent determination of Holborn and Wien at the Reichsanstalt. Should that datum, however, be shown to require revision, the validity of the present measurements would not be impaired, but new values of the melting points could be readily computed from them, which would be consistent with the better value for gold.

Al	Ag	Au	Cu	Pt
660°	970°	[1072° C.] Assumed.	1095°	1760°

The Pure Metals used were of a high degree of fineness, except unfortunately the platinum.

The gold contained less than 0.01 per cent total impurities, these being, if any, probably minute traces of silver and platinum. It was obtained as part of a specially prepared lot from the United States Assay Office in New York through the courtesy of Professor H. G. Torrey, upon whose authority the above statement is made. The purity was at least as great as the best "proof" metal used at the United States or London mints.

The silver was from the same source, and equally pure.

The aluminum was manufactured and given by the Pittsburg Reduction Company, of Pittsburg, Penn., and was stated by Mr. Alfred E.

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Hunt, President of the company, to contain but 0.07 per cent of impurity, consisting entirely of silicon.

The platinum was the ordinary platinum wire supplied by Carpentier of Paris with his Le Chatelier thermo-electric pyrometers. It presumably contained 0.5 per cent or more of impurity.

The copper was electrolytically produced, and was from the Lake Superior region. It was kindly given by Mr. Maurice B. Patch of the Buffalo Smelting Company, Buffalo, N. Y., who stated that it showed by analysis 99.99+ per cent of Cu, and contained no Ag, As, or S, and only 0.0002 per cent of Fe.

The Less Pure Metals. — Partly for the purpose of testing the effect of impurities, other samples of gold and copper were employed with the results stated later. These were: —

Dentists' Gold. — This was a gold foil employed by dentists, purchased as being of good quality.

Ingot Copper. — This was also from Mr. Patch of the Buffalo Smelting Company, who gave its analysis as

Cu	99.825
Ag	0.032
As	0.003
S	0.022
Fe	0.003
O	0.116
	100.001

This was the company's "regular run" of copper.

Commercial Electrolytic Copper. — A sample of commercial electrolytic rolled sheet copper, furnished by a friend, and not assumed to be of unusual purity. It was probably Montana copper.

Commercial Hard-drawn Copper Wire. — This was from a lot purchased for electrical testing purposes, which showed a specific resistance of 0.1440 international ohms per meter-gram, or an electrical conductivity of about 98.3 per cent referred to Matthiessen's copper.

Methods and Apparatus. — The method consists in measuring the thermal electro-motive force of a couple composed of one wire of platinum and the other of a 10 per cent rhodo-platinum alloy. One junction is immersed in the melting or solidifying metal, and the other surrounded by ice. The wire was that furnished by Carpentier of

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Paris (through Queen & Co. of Philadelphia) with the Le Chatelier pyrometer.

The emf. was measured in microvolts (international) by the Poggendorff null method modified for rapid and convenient working. The disposition of apparatus is shown in Figure 1. *B* is a battery of sufficiently steady emf. (A single Samson-Leclanché cell was entirely satisfactory.) In direct circuit with this were two water rheostats, *W*, in series; an ammeter, *A*, which was a Weston voltmeter (No. 395) with the calibrating coil only in use; and a manganine wire resistance, *a*, *b*, *c*, *d*, divided into sections, each of accurately known resistance. *T* is the thermo-couple connected through a sensitive galvanometer, *G*, and key to any desired sections of the coil *a*, *b*, *c*, *d*. The water rheostats were of about 100 ohms and 8 ohms respectively, and the vertical motion of their plungers thus served to give a coarse and fine adjustment to the resistance in the circuit.

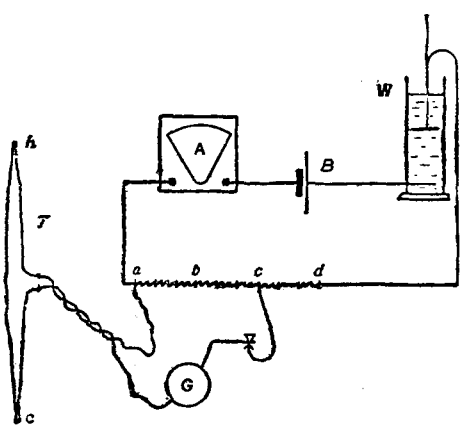

FIG. 1.

The current could thus be promptly and closely adjusted. The voltmeter was one of the type having a "calibrating coil," that is, one having a connection by means of which the usual high resistance series coil could be cut out, leaving its resistance about 117 ohms. Any of the Weston voltmeters with a special connection made to effect that result would answer equally well. The voltmeter was preferred to a mil-ammeter as probably more reliable. The instrument was carefully and repeatedly calibrated throughout its scale by an application of the Poggendorff method, measuring by the Clark cell the drop of potential in a known resistance through which a current was passing in series with the ammeter, and at the same instant reading the ammeter. The calibrations at different times checked at the same point, with an average deviation of only a few hundredths of one percent. A test for temperature error showed a change of but 0.1 per cent for a change of 15° C.; so that, as the temperature during the work was constant

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within a few degrees, no correction was needed. The manganine coil Figure 2, consisted of about 16 feet of No. 20 wire, had a total resistance of about 8.8 ohms, and was divided into nine sections by copper potential wires leading into different points along the coil. These sections were so designed that by suitably shifting the connections along *a*, *b*, *c*, etc., any thermal emf. which was to be measured could be balanced by a current which would deflect the ammeter to a point between 90 and 140 divisions (readable to tenths), — corresponding to currents from 0.006 to 0.009 amperes roughly. The coil was immersed directly in kerosene, and, as its temperature coefficient was but 0.001 per 1° C., the correction became very small. The relation and actual resistance (international ohms) of the whole coil and its several sections were repeatedly determined against a standard ohm by the differential galvanometer, and checked by a modified Wheatstone bridge arrangement. These data were reliable probably well within 0.05 per cent throughout.

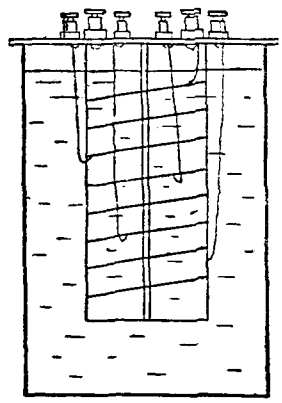

FIG. 2.

In the thermo-couple circuit, the sensitiveness necessary in the galvanometer to give the smallest emf. to 0.1 per cent was easily computed to be only about $7.7 \cdot 10^6$ (mm. defl. at 1 m. per ampere or d/c). The instrument as actually used exceeded this requirement, averaging about $5 \cdot 10^7$. Its resistance, all in series, was 14.3 ohms.

The cold junction *c* of the thermo-couple was fused together in an oxyhydrogen flame. The wires, insulated from each other by having one strung through a very fine glass tube, were run down another tube of about $\frac{1}{3}$ inch inside diameter, and 8 or 10 inches long. This tube was fused together at the bottom and top, as well as at some intermediate points, and when in use was always packed in a double vessel of cracked ice, as shown in Figure 3.

The intermediate junctions from which the copper leads went off to galvanometer and key were soldered. They were kept at an equal temperature by the device of enclosing them in a stoppered glass tube, which was packed with hair felt into a one-inch hole in a five-inch cube of cast iron. This arrangement was entirely satisfactory, but seems to possess no material advantage over making the junction of the copper leads with the Pt and Pt Rh serve as the cold junction, and

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immersing this in ice as in Figure 3, except that the latter makes a rather more bulky mass to insert in the ice.

The wires were also fused together at the hot junction except when this was unnecessary on account of their being immersed in metal. It may be noted here that, as a null method was employed, the total resistance of the thermal circuit, or any variation in it, was without effect other than a corresponding change in sensitiveness.

As the hot junction was to be immersed in vapor of sulphur as one of the known temperatures, the following apparatus was designed for this purpose. It is substantially the sulphur boiling point apparatus

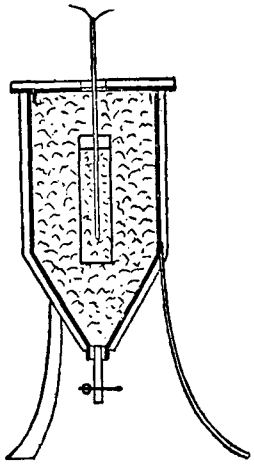

Fig. 3.

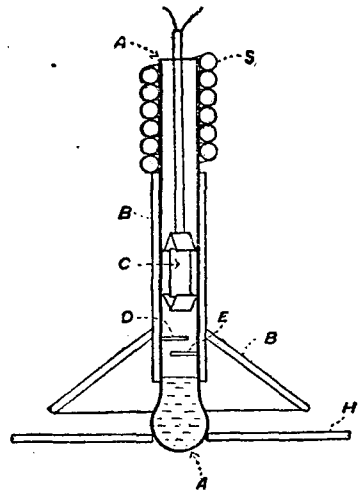

Fig. 4.

of Griffiths, and is shown in Figure 4. A glass tube, *A*, similar to the Victor Meyer vapor density tube, 16 inches long and with a two-inch bulb, was provided with an asbestos jacket and hood, *B*, *B*. The upper few inches of the tube were wound with a spiral wire spring, *S*, which rendered this part efficient as a condenser. The top was closed with a layer of asbestos. Two overlapping diaphragms of asbestos were inserted in the tube at *D* and *E*. The couple passed downward through a glass tube to the asbestos tubular hood, *C*, which served as an umbrella to shed the dripping cooler sulphur, and as a radiation screen. The hood, however, had openings top and bottom for the free circulation of the vapor. An asbestos diaphragm, *H*, upon which the bulb rested, reduced the chances of superheating.

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For the melting metals, after trial of several devices, the one shown in Figure 5 (of exactly half size) was settled upon as proving very satisfactory. The crucible *C* (usually of fire clay) is supported by clay blocks in the double-walled fire-clay furnace, *F*. A carbon block, *E*, channelled to fit the crucible, forms its cover, and a carbon diaphragm *D* inside the crucible serves to support some powdered carbon shown by the dotted mass. The object of these carbon parts was to prevent oxidation of molten metals, and they proved very effective in the case of aluminum, silver, and copper. *G G* was an

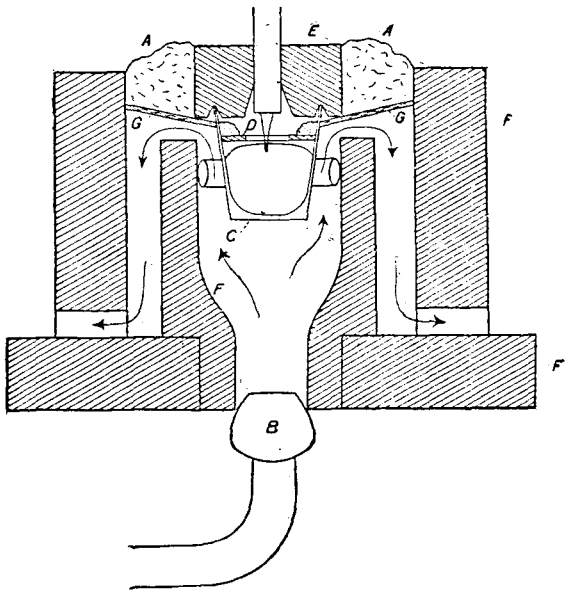

FIG. 5.

asbestos diaphragm supporting a non-conducting layer of fibrous asbestos, *A*, *A*. The temperature was controlled by the blast lamp *B*. The clay crucible was one inch in diameter outside, and the amount of metal employed ranged from 11 grams (gold) to 35 grams (copper). Larger amounts might be advantageous, but with 30 to 35 grams it was easily possible to obtain a constant indication for five minutes during the melting or solidifying of copper. No difficulty whatever was experienced with this arrangement with silver, gold, or copper. With aluminum, however, a peculiar action occurred, the cause of which in the time available for investigation could not be determined

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beyond doubt. The phenomenon was that after a few minutes of constant temperature at the melting point the indication of the thermo-couple fell off with increasing rapidity. On withdrawing the couple, cleaning it, or clipping it off and restoring it to place, the melting metal meanwhile being untouched, the indications returned to their original high value. The apparent explanation was the formation of a slag between the wires, but this was not entirely satisfactory. The use of a plumbago crucible in place of the clay, and an entirely fresh lot of aluminum, did not remove the phenomenon, and gave the same initial readings, which it could not be doubted were the ones corresponding to the melting point. The fusion of the aluminum was, however, the least sharply defined of all the metals used.

The fusion of platinum was, of course, differently effected. For this the two wires of the couple were laid close together on a piece of lime. An oxy-hydrogen flame was then directed upon their ends, and the platinum fused into a globule which with care could be made to travel slowly up the wire. There was no difficulty in obtaining steady temperatures for a sufficient period to make the necessary readings, and check results to 0.1 per cent were obtained on different days.

The galvanometer, keys, coils, and all junctions of dissimilar metals, were, so far as possible, covered with boxes of wood, pasteboard, or asbestos, to maintain uniformity of temperature, and thus minimize local thermo-electric disturbances. With this precaution no sensible trouble from that source was experienced.

The procedure is as follows. To take the observation for vapor of sulphur, for instance, the hot and cold junctions are exposed as described. After a sufficient time the main circuit is closed, the thermal circuit is connected to a suitable part of a, b, c, d, and the rheostats, W, are adjusted until on pressing the key no deflection occurs in the galvanometer, G. At this instant, A is read, which gives the current c in the main circuit. The adjustment is disturbed and remade a number of times, and the resulting readings should check to the nearest tenth of a division of A, provided the metal has reached a steady state of temperature.

By this adjustment the drop of potential $c\,r$ due to the current c amperes in the part r ohms of the resistance a, b, c, d, spanned by the thermal circuit, is made equal to the total resultant emf. in the thermal circuit. The latter, which will be denoted by $\Sigma_c^h e$ or $\Sigma_o^l e$, is the algebraic sum of the thermal emf. proper of the junctions of the Thomson emf. in the wires, and of any "stray" or local thermal emf.

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in the circuit. The last was found to be negligible throughout the work.

To observe the melting point, the furnace containing the metal is heated more or less rapidly until the melting point is approached. The blast lamp is then adjusted to give a slowly rising temperature. The thermal circuit, with the couple previously fused into the metal, is connected to a suitable section of a, b, c, d. The rheostats are continually adjusted for zero deflections of the galvanometer, G, and the corresponding readings of A are taken. These will show gradually increasing values, but the rise will presently be interrupted by a series of constant readings, after which the readings, will again steadily increase. This period of constant, or nearly constant, readings of A is that in which the latent heat of fusion is being absorbed, and its duration is frequently several minutes. The temperature at that time is, of course, that of the melting point. The reverse process, starting with the metal in a molten state and cooling it gradually, shows a similar period of solidification.

No difference was discovered between the ascending and descending readings when a sufficient amount of the metal and a slow rate of heating and cooling were employed. With small amounts the steady reading was more or less masked by phenomena which were clearly due to inequality in distribution of temperature throughout the mass of mixed liquid and solid metal. In the case of aluminum, however, something more than this irregularity was observed, as elsewhere stated, but the time at command did not permit a study beyond the point of satisfying ourselves that the point observed was unquestionably the true melting point.

This work was done chiefly as the thesis work of Messrs. Lawrence and Barr. The efficient assistance of Mr. C. L. Norton contributed materially to its progress and success.

The computation of temperatures t from the observed electro-motive forces Σe involves a knowledge of the function connecting the two, i. e. of the function

$$\Sigma_0^t e = f(t) \quad \text{or} \quad t = F(\Sigma_0^t e).$$

This problem has been elsewhere discussed by one of the authors of this paper.*

In that article two interpolation formulæ were developed. They were respectively of the following forms, applying to the case where

* Holman, These Proceedings, *ante*, p. 193.

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one junction of the couple is kept at 0° C., and the other is at any other temperature t C., or $\tau = t + 273°$ absolute; m and n are constants, different for the two expressions; $\Sigma'_0 e$ denotes the resultant thermal emf. of the circuit, viz. that which is the object of direct measurement. The first, called the exponential equation, is

$$\Sigma'_0 e = m\,\tau^n - \beta \quad (\text{where } \beta = m\,\tau_0^n = m \times 273^n).$$

The second expression, called the logarithmic equation, is

$$\Sigma'_0 e = m\,t^n, \quad \text{or} \quad \log \Sigma'_0 e = n \log t + \log m.$$

Both formulæ have been applied to the data of the present investigation given in Table I., with results shown below. The Avenarius formula has also been applied for purposes of comparison.

To evaluate the constants m and n of the exponential equation (for method, consult the paper referred to) it is necessary to have values of $\Sigma'_0 e$ at three known temperatures. Of these, however, one may be $\Sigma'_0 e = 0$, at $\tau = 273°$, i. e. with both junctions in ice. It therefore remains to fix upon two other temperatures between which to interpolate, or, in other words, two other temperatures which shall be assumed as known. In looking over the ground it seemed that the boiling point of sulphur, being so high and so accurately determined by Callendar and Griffiths,*

$$444.53 + 0.082\ (\mathrm{H} - 760),$$

was pre-eminently one of these points. The other must be much higher, and the melting point of pure gold seemed to be almost, if not quite, the only one upon which reliance could be placed.

Apart from freedom from oxidation, and its conveniently high point of fusion, gold seemed the more suitable because its melting point had recently been so carefully measured by Holborn and Wien, and because the metal could be obtained of the necessary purity. Add to these considerations the fact that its melting point in a state of at least fairly high purity has been measured by more experimenters than that of any other high melting metal, so that it serves as an excellent connecting link between their work, and we have claims which no other substances can at present offer. The fusion point of gold was therefore chosen as the second reference or calibration temperature. As to the figure to be assumed as the melting point of gold there is room for differences of opinion. The claims of the work

* Phil. Trans. CLXXXII, 119, 157 (1891).

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of Holborn and Wien, supported to some extent by considerations advanced by Barus,* lend much weight to the conclusion that Violle's value of 1035° is considerably too low. Granting this, and in the absence of sufficient basis for the assignment of weights to the work of divers other investigators, the simplest and best step seemed to be to adopt provisionally, without modification, Holborn and Wien's value,

$$1072°.$$

These two points settled upon, the constants m and n could be computed as elsewhere described, and the equation transposed to deduce other values of t from observed values of $\Sigma_0' e$. Representing $m\,\tau_0^n$ by β, a constant, the equation for the temperature as a function of $\Sigma_0' e$ takes the form

$$t = \sqrt[n]{\frac{\Sigma_0' e + \beta}{m}} - 273°,$$

which is, of course, easily solved by logarithms.

The data given in Table I. yield the values $m = 0.3901$, $n = 1.488$, $\beta = 1645$, in international microvolts and degrees centigrade, so that

$$\Sigma_0' e = 0.3901\ \tau^{1.488} - 1645, \quad \text{or} \quad t = 1.488\sqrt{\frac{\Sigma_0' e + 1645}{0.3901}} - 273.$$

From these the temperatures of column six have been computed.

The constants of the logarithmic formula have been computed from the same data for sulphur and gold, the method being sufficiently obvious. The equation becomes

$$\Sigma_0' e = 2.49655\ t^{1.2563}.$$

The corresponding melting and boiling points are given in Table I., column seven.

Substitution of the same data in the Avenarius equation yields

$$\Sigma_0' e = (t_h - t_c)\ \{9.7335 + 0.00\,484\,49\ (t_h + t_c)\}.$$

The corresponding melting and boiling points are given in column five.

Provisional Values of Melting Points.

In the paper referred to it was shown, 1st, that the logarithmic expression fitted the Barus comparisons of the irido-platinum couple with the air thermometer within the limits 400° to 1200° C. with no

* Am. Jour. Sci., XLVIII. 336.

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sensible systematic error; 2d, that the exponential equation similarly fitted the Holborn and Wien comparison of the rhodo-platinum couple with the air thermometer within the same limits; 3d, that the exponential equation diverged systematically, although slightly, from the Barus data, and the logarithmic from the Holborn and Wien data, by about equal and opposite amounts both inside and outside these limits, but much more markedly between 0° and 400° than at higher points.

TABLE I.

MELTING POINTS.

Date.	Subst.	Σe Micro-volts.	Temperatures.					
			Assumed as Correct.	From Aven. Eq. t_a.	From Exponent Eq. t_e.	From Log Eq. t_l.	$\frac{t_e + t_l}{2}$	Provisional Values.
3–?	H_2O	885.8	99.64°					
4–10	H_2O	890.4	100.57					
		888.1	[100.10]	87.4°	91.7°	107.3°	99.5°	
3–15	$C_{10}H_8$	2213	218.3					
3–23	$C_{10}H_8$	2224	218.9					
3–25	$C_{10}H_8$	2216	218.2					
		2218	[218.5]	206.6	211.4	222.4	216.9	
3–?	S	5287	444.7					
3–22	S	5289	445.2					
3–29	S	5287	444.5					
		5288	[444.8]					
4–24	Cu	16463	—	1095.	1095.0	1096.5	1095.5	1095
4–29	Au	16002	[1072]	—	—	—	—	[1072]
4–29	Ag	14093	—	975.	972.	969.	970.5	970
5–2/3	Pt	30313	—	1695.	1735.	1783.	1759.	1760
5–3	Al	8638	—	665.5	662.5	656.2	659.4	660

Aven. $\Sigma_0^t e = (t_2 - t_1)\{9.7335 + 0.00\,484\,49\,(t_2 + t_1)\}$.

Exp. $\Sigma_0^T e = 0.3901\,\tau^{1.488} - 1645$.

Log. $\Sigma_0^t e = 2.49655\,t^{1.2563}$.

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Inspection of columns six and seven, Table I., will show that the computed boiling points of water and napthalin by the exponential and logarithmic equations depart widely from the known temperatures in opposite directions, by about equal amounts, and in the directions according with the departures from the Barus and Holborn and Wien data. Also, that the differences between the computed melting points intermediate between sulphur and gold differ but slightly by the two formulæ, thus confirming the former conclusions. It is obvious, therefore, that although either of the two formulæ would yield fairly good interpolations for Al, Ag, and Cu, yet that a mean between the two would probably quite nearly offset against each other the systematic errors of the respective equations. This is also true in the dangerous process of extrapolation for the platinum melting point, where the chances of error in the result seem to be probably very much reduced by averaging. The means of the melting points computed by the exponential and logarithmic equations are, therefore, regarded as the nearest available approximations, and the round numbers of column nine are adopted as provisional values to represent the results of the work.

Comparison of the results of the Avenarius formula, column five, will show that they depart widely from the others in the direction which would have been anticipated from the conclusions of the previous paper, thus further strengthening those inferences.

In addition to the foregoing, the melting points of three other samples of copper, and one other of gold, were measured. The gold was dentists' gold "foil," purchased in Boston. This is usually classed as "very nearly pure," but its analysis was not known. No special interest, therefore, attaches to it beyond the indication that it gives of the sign and order of magnitude of the error (about —4°) which would be introduced by the use of such gold in the calibration of the Le Chatelier pyrometer, or in similar ways.* The melting point was found to be 1068°.

The four coppers yielded the appended results.

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* Holman, Calibration of the Le Chatelier Thermo-electric Pyrometer. See These Proceedings, *post*, p. 234.

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TABLE II.

$\Sigma_0^t e$ Microvolts.	Melting Points, C.	Purity of Metal.	Description.
16463	1095.0°	99.99+ %	Electrolytic. Probably Lake Superior copper, Buffalo Smelting Co.
16448	1094.3	99.83	Ordinary ingot. Same source.
16456	1094.7	Unknown.	Electrolytic. Probably from Montana.
16446	1094.2	Unknown.	Commercial hard drawn wire from Washburn and Moen Co. Sp. Elect. Conductivity (referred to Matthiessen value) 98.3 per cent.

The concordance of these results on various coppers, together with the completely satisfactory behavior of the metal in fusion, and the ease and cheapness of obtaining the metal of a very high grade of fineness, suggest the decided availability of copper in a direct study of high temperatures or melting points by the gas thermometer. A large mass of the metal could be employed, and a constant and uniform temperature for a protracted period thus secured for the bulb of the gas thermometer, or for other apparatus immersed in the molten or solidifying material. There are unfortunately too few substances which fulfil even these requirements. An added merit lies in the nearness to the gold melting point, enabling the two to be satisfactorily connected by some means of relative measurement.

It also appears that the use of good commercial copper would introduce sensibly less error (3° less) into the calibration of the Le Chatelier pyrometer than the use of the "dentists' gold" above tested, which is as good metal as would readily be obtained in the market by most observers.

Reliability of the Results. — The points involved are: —

Instrumental errors.

Purity of the metal.

Was the observed point the real melting point?

Validity of the interpolation equation.

Error in the assumed melting point of gold and boiling point of sulphur.

The investigation was planned and the apparatus arranged with the intention of reducing the combined instrumental errors below one

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tenth of one per cent in the measurement of Σe above 200° C. Tests, check measurements, and a discussion of the sources of error, unnecessary to detail here, have given satisfactory demonstration that an even higher accuracy than this was attained. As far, therefore, as constant or variable instrumental errors are concerned, it is believed that no error beyond 0°.5 to 1° C. exists in the results, while probably this estimate is large.

The error from impurities must have been exceptionally small, as the analysis of the metals indicates. Some impurities from alloying with the platinum and rhodium of the thermo-couple must have entered during the experimenting, but as results at different stages of the work checked those obtained upon the first use of the metal, and as renewals of the metal made no difference in readings beyond the limits of other variations (about 5 parts in 10,000), the error from this source must have been negligible.

In the case of platinum the metal at command was unfortunately not of known composition, nor was it possible at the time to obtain any whose purity was known. An analysis of the wire used may perhaps be obtained later, and it is hoped to carry out further measurements with the better platinum now obtainable through the recent advances made in its manufacture in Germany and England.

The aluminum was of very high grade, but it is thought that still better may be obtained, and the peculiar occurrence attending its melting point measurements should be further investigated.

The actual effect of the small impurities cannot be numerically estimated, but must have been inconsiderable except for platinum, where the error probably has the positive sign.

As to the third point, there was no reasonable doubt left in the minds of the observers that the observed temperatures were sensibly the melting points. Except as noted for aluminum, the readings with rising and falling temperatures did not exceed about one part in one thousand. Also entirely independent observations on separate days, and with renewals of the metals in some cases, were equally concordant. The average difference was much less than the error of reading the ammeter. As an example of the concordance, and at the same time as showing the homogeneity of the thermo wire, three calibrations in sulphur are quoted in Table III.

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TABLE III.

Date.	Σe Microvolts.	Computed Temperature of Sulphur.	Σe reduced to 445°.
March ?	5287	444.73°	5290
March 22	5289	445.18	5287
March 29	5287	444.53	5293

Between these observations a considerable length of the wires was necessarily clipped off. Reduced to a common temperature of 445°, the maximum difference is but 6 microvolts in 5290, or 0.11 per cent, while the average deviation of a single observation is but 0.02 microvolts, or 0.04 per cent, and of the mean but $0.02/\sqrt{3} = 0.012$ microvolts, or 0.024 per cent. At higher temperatures the discrepancy was even smaller.

The validity of the interpolation formulæ has been already discussed. A statement of the extreme error which may have been introduced into the results by this source should however be added. This is believed to be for aluminum less than $\pm 2°$, for silver less than $\pm 2°$, for copper less than $\pm 0.5°$, and for platinum less than $\pm 10°$.

Comparison with the temperatures computed by the Avenarius equation show errors by the latter to be about 1.5 times as great for water and naphthalin, and of the same signs. It is therefore much less reliable, especially for the platinum temperature, and no weight is attached to its results.

Melting Points by various Authorities. — A collection of these is given in Table IV. Except in the case of the Barus data, the results are set down directly as given by their authors. A further discussion of these with reference to the purity of the metals used, and the characteristic errors of the methods employed, would doubtless prove instructive, and might partly remove or account for some of the apparent discrepancies, — a task which will perhaps be undertaken later.

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TABLE IV.

Authority.	Date.	Method.	Metals.				
			Al	Ag	Au	Cu	Pt
			°	°	°	°	°
H., L., and B. . . .	1895	Th.-el.	660	970	[1072]	1095	1760
Violle	1879	Sp. Ht.		954	1035	1054	1775
Ledebur	1884	Sp. Ht.		960		1100	
Le Chatelier		Th.-el.	635		[1035]		
Callendar				[945]	1037		
Erhard and Schertel .				954	1075		
Barus, by Log. Eq.* .	1894	Th.-el.	641	985	1060	1095	1783
" by Eq. 3 . . .	"			986	1091	1096	1757
Holborn and Wien . .	1892	Th.-el.		968	1072	1082	
Mean of independent absol. meas'ts, i. e. exclud. H., L. & B., Le C., and C.			641	964	1068	1083	1779

N. B. — Values in brackets [ ] are those assumed by the observers, and upon which their other values depend to a greater or less extent.

* See discussion by Holman, *ante*, p. 193.

ROGERS LABORATORY OF PHYSICS,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
Boston, October, 1895.

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Investigations on Light and Heat, made and published wholly or in part with Appropriation from the Rumford Fund.

XII.

CONTRIBUTIONS FROM THE PHYSICAL LABORATORY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.

XLVI. — PYROMETRY: CALIBRATION OF THE LE CHATELIER THERMO-ELECTRIC PYROMETER.

By Silas W. Holman.

Presented November 13, 1895.

In a discussion of thermo-electric interpolation formulæ * the author has shown that the resultant thermal emf. $\Sigma_o^t e$ of a closed metallic circuit of two metals, with one junction at 0° C. and the other at t° C., could be expressed to 0.5 per cent or better above 300° C. by an expression of the form $\Sigma_0^t e = m\, t^n$ or $\log \Sigma_0^t e = n \log t + \log m$, where m and n are constants depending on the metals of the couple. Similar demonstrations show that with the cold junction constantly at 20° C. the emf. may be expressed by $\Sigma_{20}^t e = m\, t^n$ nearly enough. This fact, together with the known fact that the D'Arsonval galvanometer gives readings nearly proportional to the currents, and therefore to Σe on a circuit of constant resistance, led to the thought that the calibration of the Le Chatelier thermo-electric pyrometer might be simplified by the use of a logarithmic instead of a direct plot. A study of a series of six calibrations made at different times by four different sets of observers, with two distinct pyrometers, and in nearly every case with different suspension wires and adjustment, confirmed the deduction and led to the following method. It will be seen that the method requires calibration at only two known temperatures, instead of several, as formerly, — a saving of labor and a gain in accuracy. The method, although suggested by the facts referred to, is not merely a deduction from them. It should rather be regarded as an empirical process based on experiment. It is not rigidly exact, viewed from either a mathematical or experimental standpoint, but is merely an approxi-

* Thermo-electric Interpolation Formulæ, *ante*, p. 193.

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mation holding within the limits of variable error of the instrument, and probably well within the limits of uncertainty of the assumed values of the melting points employed in calibration.

For clearness, the usual method of calibration will be first stated, and then the proposed method.

Usual Method.

The cold junction is kept at a temperature usually about that of the room, and measured by a mercurial thermometer. The spot of light is made to read zero with the circuit open. The hot junction is then exposed successively to several known high temperatures, and the scale readings are taken. These temperatures are, ordinarily, the boiling points of naphthalin ($C_{10}H_8$), and of sulphur, the melting points of aluminum, gold, and platinum, — selected as being the most satisfactory in manipulation, and reliable in value. The values assumed for these points differ, following the judgment of the experimenter, Violle's figures 1775° C. for platinum and 1035° or 1045° C. for gold, and Le Chatelier's 625° or 635° for aluminum, being most commonly accepted. From measurements and considerations elsewhere * discussed, the author recommends the following as provisional numbers in preference to the foregoing values.

$C_{10}H_8$	$218.7 + 0.0625\,(H-760)$	Crafts,† Holman and Gleason.‡
S	$444.53 + 0.082\,(H-760)$	Callendar and Griffiths.§
Al	660.	Holman, Lawrence, and Barr.*
Ag	970.	" " "
Au	1072.	" " "
Cu	1095.	" " "
Pt	1760.	" " "

A plot is then made with deflections (scale readings) as abscissas (horizontal) and temperature differences $(t - c)$ between the hot and cold junctions as ordinates (vertical). The points thus obtained lie along a curve which in the upper part approaches somewhat closely to a straight line. But it is nowhere exactly straight, and the error of assuming it so may amount to 10° or 15° or even more. On the other hand the points lie so far apart, if plotted upon a scale com-

* Holman, Lawrence, and Barr, *ante*, p. 219.

† Crafts, Bull. de la Soc. Chim., XXXIX. 196, 277 (1883).

‡ Holman and Gleason, Proc. Amer. Acad., XXI. 237 (1888).

§ Calendar and Griffiths, Phil. Transact., CLXXXII. 119, 157 (1891).

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mensurate with the sensitiveness of the instrument, that it is impossible to draw a curve through them which shall be much more reliable in the upper parts (the portion most frequently needed) than the straight line. Although this statement is perhaps counter to others that have been made on the subject, it is the author's opinion, arrived at after prolonged experience with the instrument.

In subsequent temperature measurements this curve is, of course, used for interpolation in the customary manner; that is, any deflection being observed, and at the same time the temperature c' of the cold junction, the plot is entered with this deflection as abscissa, and the corresponding ordinate of the curve is read off. This ordinate will be approximately $(t - c')$ the temperature of the hot minus that of the cold junction. Hence the desired unknown temperature t is obtained approximately by adding c' to this ordinate.

Proposed Method.

Observations. — The scale is adjusted so that the spot reads zero with the circuit open. The cold junction is kept at a temperature about that of the room, and measured by a mercurial thermometer. In careful work this temperature should be kept constant, or nearly so, either at 20°, or, better, at 0° C. The other junction is then exposed successively to two known temperatures, *preferably boiling sulphur and melting copper* (for reasons to be given), or, if temperatures upwards of 1200° C. or 1300° C. are chiefly to be measured, to melting copper and melting platinum. Deflections and temperatures of the cold junction are taken.

Correction for Cold Junction. — If the cold junction is always kept within about one degree of a constant temperature $c°$, e. g. 20° (or 0°), both in calibration and subsequent work, these observed deflections require no correction. If that is not the case, then the deflection should be corrected to obtain what it would have been had this been done. This is readily effected as follows. Let a be the change of deflection per degree at 20° C. This may be found nearly enough by observing once for all the deflection with the cold junction at some observed temperature, anywhere from 10° to 15°, and the hot junction at an observed temperature from 30° to 40°. The deflection divided by the temperature difference will, of course, be a. Then if the observed temperature of the cold junction in a measurement is, e. g., 16° instead of 20°, the correction would be $(20 - 16)\ a = 4\ a$, to be subtracted from the observed deflection, since that was obviously too large. These corrections are small, and can easily be

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made mentally, since a is seldom more than one twentieth of a small division of the scale.

Calibration, and Computation of Unknown Temperature. — Let d_s represent the corrected deflection for the sulphur temperature t_s (computed from the reduced barometric pressure H at the time by the foregoing formula) and let d_c be that for the assumed melting temperature t_c of copper or the metal used. Plot two points with log d as abscissa and log t as ordinate respectively. Draw through these two points a straight line. Then within the limits of error of the apparatus, *the ordinate of this line corresponding to any abscissa* log d *will be* log t, *the log of the desired temperature* of the hot junction, d being any observed deflection corrected to 20° or 0° as above. That is, the number corresponding to this logarithm will be t.

By far the most convenient way to effect this plotting and subsequent interpolation, instead of employing logarithm tables and the ordinary co-ordinate or plotting paper ruled with equidistant lines, is to use plotting paper with a logarithmic ruling, that is, with lines spaced at distances progressively diminishing according to the logarithmic law, like the divisions of the ordinary slide rule. By suitably numbering the axes of such a sheet the desired quantities can be plotted directly without the aid of the logarithm tables. Subsequent interpolation then becomes exceedingly easy, since it is merely necessary to enter the plot with the corrected deflection as abscissa, and read off the corresponding ordinate on its numbered axis, this giving directly the unknown temperature t. Unfortunately such paper (which would be useful in many physical and practical problems) is nowhere on sale so far as the author is aware.

In default of such paper, and instead of using the plot of logarithms for continuous interpolation, a direct reading plot of deflections and temperatures may be made from it once for all. On the logarithmic plot look out the ordinate for every ten (or twenty) divisions of the scale, i. e. corresponding to log 10, log 20, log 30, etc. (smallest divisions). Look out in the log tables the numbers corresponding to these ordinates, thus obtaining t_{10}, t_{20}, etc. Make a new plot, with 10, 20, 30, etc. as abscissas, and t_{10}, t_{20}, t_{30}, etc. as just found, as ordinates. These points can be taken at such short intervals that a reliable smooth curve may easily be drawn through them, and this is then available for subsequent direct interpolations.

In the absence of logarithmic plotting paper, log plots may very conveniently be made by a straight edge, graduated with a logarithmic scale. Four of such rulers (two of single and two of double scale)

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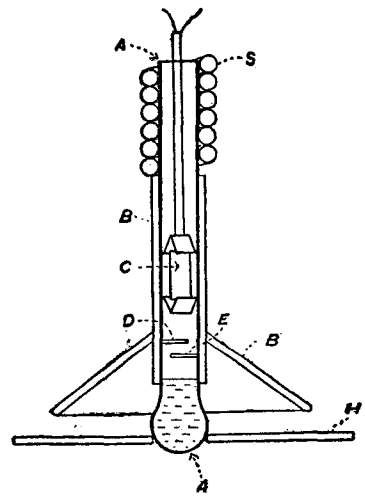
may be cut from an ordinary boxwood slide-rule by a skilful carpenter. They are very useful in a variety of physical work, but less so than the ruled paper.

Proof of the Method. — The method rests for demonstration on the fact that logarithmic plots thus made for the six calibrations above cited, each containing observations on naphthalin, sulphur, aluminum, gold, and platinum, and using the above temperatures, were straight lines well within the limits of variable error of the observations with but one exception, when the platinum point showed a wide divergence, presumably due to mistake, or possibly to faulty setting up of the instrument.

Apparatus and Procedure in Calibrating: Sulphur. — For this boiling point, in order to obtain as good results as the instrument is capable of, the boiling point tube shown in the sketch is satisfactory, and a duplicate serves well for naphthalin. The glass tube is about an inch in diameter, and twelve inches long, terminating below preferably in a bulb about two inches in diameter. The tube, to within two inches of the top, is wrapped with asbestos cloth of a thickness of at least a quarter of an inch, to prevent radiation and superheating. An asbestos cover closes the top. The clear part of the tube serves as a condenser, which may be made more efficient by a spiral coil of wire, *S*. It is easy to regulate the rate of boiling so that the visible line of condensation in the tube is nearly steady in position. The bulb rests on a diaphragm of asbestos board, having an opening about half an inch smaller in diameter than the bulb. The whole apparatus is supported in a clamp stand. The flame plays upon the bulb where it is exposed by the hole, but the diaphragm (six or eight inches in diameter) prevents the hot gases from passing up around the tube, which would cause superheating. Two overlapping diaphragms, *D* and *E*, about an inch above the sulphur and half an inch apart, prevent spattering and radiation from the liquid to the thermal junction. The wires of the couple extend downward through the cover to a



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point an inch or less above the diaphragm. The sulphur should extend from the bulb to a point half an inch or more into the tube. It will usually be found necessary to pour out the liquid sulphur at the close of a calibration to avoid breaking the tube at the next heating. If there is trouble from breaking of the tube during boiling (none with good glass) a wire copper gauze wrapped about the bulb will be found a preventive. The boiling should be maintained for a few minutes after the sulphur vapor has risen above the top of the asbestos to insure uniformity of temperature. It is advantageous to put the wires through a small hood, or umbrella of asbestos at a point about an inch above the junction, so shaped as to shed the drip of cooler liquid sulphur which will run down the wires. A special form of this hood is shown at *C* in the figure. Both this and the diaphragms in the tube are, however, unnecessary in ordinary work.

For comparatively rough work it is sufficient to boil some sulphur in an ordinary or small test tube (about one fourth full) and hold the junction at the surface of the boiling liquid, taking pains not to have it touch the tube, and also not to overheat the tube. This is the customary procedure, but is not quite worthy of the instrument.

The barometer and its temperature should be observed at the time and place of making the calibration, although the errors from omission of this are negligible in rough work.

Copper. — The high grades of commercial copper are good enough* for this use; such, for example, as are used in the best rolled sheet copper and wire. This, of course, is easily obtainable and inexpensive, and may probably be relied upon as having a melting point not much, if any, over 1° C. below that of pure copper. Electrolytic copper of a much higher grade of purity is preferable, and is not now rare or expensive.

A fire clay crucible,† 1¼ to 1½ inches deep, and about 1 inch in diameter, is held in place inside a small furnace by pieces of fire-clay, as shown on page 240. A double-walled furnace of the design and proportions shown ‡ (the figure is half size) is most satisfactory. It is about 4½ inches outside diameter, and 3½ inches high. The crucible contains upwards of fifty grams of copper. Above this, within

* See results by H., L., and B.

† Buffalo Dental Co., Buffalo, N. Y.

‡ Wiesnegg, also Carpentier, both of Paris, supply such a furnace; or one may readily be made by any manufacturers of fire-clay apparatus. The Fletcher furnaces may also be used but are not so convenient for the purpose because the products of combustion escape at the top.

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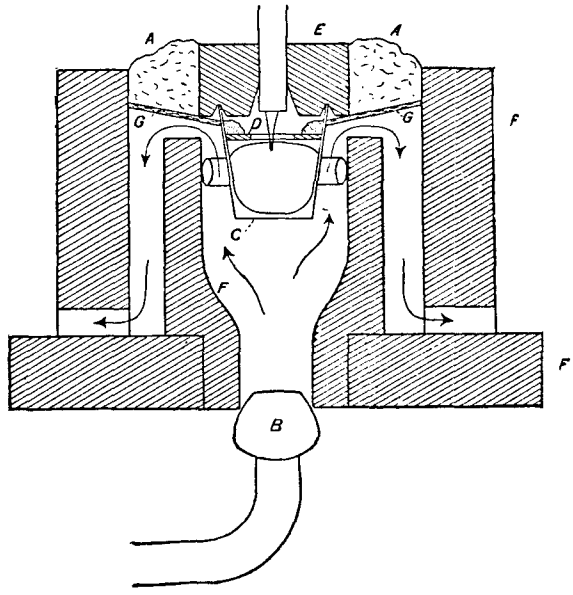
the crucible, is a diaphragm, *D*, made from a plate of battery carbon. It has a central perforation large enough to permit the passage of the clay tube carrying the thermo-couple. Upon this diaphragm is placed powdered charcoal. A block, *E*, of battery carbon is turned to fit the rim of the crucible somewhat closely to serve as a cover. *G* is a diaphragm of asbestos board which deflects the gases, and upon this at *A* is placed fibrous asbestos to reduce the heat conductivity. The cover belonging to the furnace is not used. Simpler details might serve sufficiently well, but they must effect the same result,



namely, to produce by slow combustion an atmosphere of carbon dioxide in the crucible to retard the oxidation of the copper. As above arranged, the powdered charcoal does this, and the carbon plates do not burn.

The thermo-couple projects as shown into the metal, being of course thrust in during the first melting. It is obviously indifferent whether the wires are joined or not. The end of the wires will require clipping subsequently, to remove the short section injured by action of the copper. The uniformity of the wire, however, renders this a source of no sensible error.

The apparatus being arranged as shown, and the copper liquefied

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(it should not be unduly superheated), the blast is slightly reduced so that the crucible may cool slowly, and the pyrometer is read continuously. When the solidifying point is reached, the reading will become constant for some minutes (dependent on the rate of cooling) and will then begin to descend. This "steady point" occurs, of course, during the absorption of the latent heat, and is the desired reading corresponding to the solidifying point. The blast is then increased, and the corresponding constant reading in the ascending temperatures gives the melting point. This should, with copper, be sensibly coincident with the solidifying point, and will be found so unless complications are introduced, through too rapid heating or cooling, or through the formation of slag upon the top of the copper. It is well to withdraw the junction, clean it if necessary, and take check readings.

The advantages of copper over gold, as demonstrated elsewhere,* are that it is more easily and cheaply obtainable in a state of purity insuring a reliable melting point, and that, by using a large mass, an unmistakable steady reading of considerable duration can be obtained. The latter consideration is of special weight where the galvanometer is exposed to jarring, or the observer is not experienced. The operation is no more laborious, and, except possibly for a skilled observer, is less time-consuming, and more satisfactory than the customary method with gold.

In Le Chatelier's original method of employing gold (or other metals) this same furnace was used, but with its cover on. The crucible, without a cover, was filled with magnesia or lime, and the thermal wires, passing through a perforation in the furnace cover, terminated with their junction in the centre of the crucible, surrounded by the magnesia. Before its insertion the junction was carefully wrapped with a small piece of wire or foil of gold, or of any metal under test. This being arranged, the blast was controlled to raise the temperature at a slow and steady rate. The spot of light on the pyrometer scale was then watched closely. It would be seen to advance steadily until a certain point was reached, then to stop abruptly for a moment, then to start upward again almost with a bound and go on rising. This temporary stopping was due to the time required for the absorption of the latent heat of fusion. A similar stopping point may then be generally observed on allowing the furnace to cool slowly. These two points, the "melting and freezing points," should

* See former reference to H., L., and B.

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in general agree. With too rapid rates of heating or cooling, they are likely to show an erroneous disagreement. Under favorable conditions, namely, with the galvanometer in a place free from jarring, and with a steady air-blast of quite sufficient capacity, this method yields perfectly good results, although the inexperienced observer will generally miss the reading on the first one or two trials. But in most places, notably in connection with industrial plants, it is not infrequently difficult or impossible to secure the necessary steadiness of support or of blast. Failing these, the stopping point sought is very likely to be so masked by irregularities in the motion of the spot as to introduce much uncertainty into readings, if not entirely to prevent satisfactory calibration by this method.

Another way is to have the two thermal wires held together at the ends merely by the wrapping of gold, etc., and under slight tension, so that as soon as the metal melts the wires will draw apart and open the circuit. The spot will then reach a highest point corresponding to the melting point, and then suddenly drop to zero. In practice this method, although convenient in some cases, has been found not to yield satisfactory results on the whole.

With some metals, particularly those melting below gold, the author has found the following arrangement to work well, being more rapid and under better control. A small crucible of fire-clay, 1½ or 2 inches long, and ¼ to ⅜ inch inside diameter, with straight sides and a flat bottom, is employed.* Into this is inserted the clay tube carrying the wires, a packing of asbestos being used around it, if it does not pretty well fit the crucible. The junction remains free about half an inch from the bottom and not touching the sides. The crucible is then gradually heated in the flame of the blast lamp, and the stopping point observed as before.

Platinum. — For this we depend on the direct fusion of the platinum wire of the couple just at the junction.† A convenient way is to fuse the ends together, then to bend the wires so that the two lie closely side by side, and are nearly straight, but not touching. Then lay the end on a smooth surface of quicklime. A small flame from the oxyhydrogen blowpipe is then directed upon the junction. The globule at the end will fuse, and may gradually work up along the

* Made to order by Hall and Sons, Tonawonda St., Buffalo, N. Y.

† It may be of interest to others, as it was to the writer, to learn that the firm of Heraeus of Hannover, Germany, which has made platinum of exceptional purity for the Reichsanstalt, has an agency in New York, Charles Englehard, 41 Cortland St., N. Y.

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wires. By watching the surface appearance of the globule closely, it is easily possible to control the position and effect of the flame so as to maintain the mass just on the point of fusion and get a fairly constant reading. Heavily clouded dark glasses *must* be used in watching the platinum. Neglect of this involves risk of serious permanent injury to the sight, and, if persisted in, of even greater danger.

Modifications of the Le Chatelier Thermo-electric Pyrometer. — By an experience extending over four years in the use of this instrument in its original form, and after tests and study of many other forms of pyrometer, the writer is convinced both that the thermo-electric method is by far the most promising one as the basis for industrial pyrometer, as well as for much measurement in scientific research, and that the Le Chatelier form of the instrument is the most generally satisfactory one now obtainable on the market. Yet for general industrial services the Le Chatelier instrument falls short of the requirements in two ways. First, it is not sufficiently simple of manipulation in the setting up, and in the calibration, to be put into the hands of any but a fairly well trained observer. A trained chemist of works, an educated superintendent, or any man of such caliber may be expected to take the instrument as sent by the makers, mount it, and operate it successfully; and under such observers it is doing important service in many places. The mere reading can be done by any foreman after a few words of explanation. Secondly, the conditions of support requisite for the galvanometer, although often obtainable, are by no means commonly to be found in those portions of industrial works where it would be otherwise advantageous to locate the instrument. These facts are restricting the introduction of an instrument otherwise excellent in its performance and marking a distinct onward step in the art of practical pyrometry.

The urgent need of a still more universally practicable pyrometer cannot be too strongly nor too often emphasized. In a large number of industrial processes of great magnitude the employment of a reliable pyrometer would certainly result in a notable advance in quality of product, in prevention of waste, in improvement or perfection of the process itself, and in the discovery of new methods and new products. If a galvanometer as reliable, as simple, and as portable as the Weston magnetic voltmeter could be directly connected to a rhodo-platinum thermal couple, there would result, as I have for some years urged, an almost ideal pyrometer for technical work. Thus far, unfortunately, the Weston instruments do not yield in this combination sufficient sensitiveness to admit of their being put forward as meeting

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any but very special needs. Nevertheless, at least one such combination is said to have been successfully used for a certain purpose. The writer has made repeated efforts to obtain a suitable instrument from the Weston Company, and from some others, without success.

Rogers Laboratory of Physics,
Massachusetts Institute of Technology,
Boston, September, 1895.

NOTE.

A portable form of D'Arsonval galvanometer, combined with a rhodo-platinum thermo-couple and graduated in degrees up to 1500° C., is now announced by Keiser and Schmidt of Berlin.* Its graduation is based upon the investigations of Holborn and Wien at the Reichsanstalt.

The author desires, also, to call attention to the convenience of maintaining a constant calibration curve for the Le Chatelier pyrometer by the insertion of an adjustable resistance in the circuit. By this means the unavoidable slight changes of resistance of the circuit, of sensitiveness of the galvanometer, and even of electro-motive force of the couple, can be readily offset. The procedure would, of course, be to adjust the resistance until the sulphur or the copper reading was the same as in the original calibration. S. W. H.

* Zeitschrift für Instrumentenkunde, XV. 285 (August, 1895).

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Investigations on Light and Heat made and published wholly or in part with Appropriation from the Rumford Fund.

XIII.

CONTRIBUTIONS FROM THE PHYSICAL LABORATORY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.

XLVII. — CALORIMETRY: METHODS OF COOLING CORRECTION.

By Silas W. Holman.

Presented November 13, 1895.

The following general method of treating the cooling correction is applicable to nearly all non-continuous calorimetric processes, such as the measurement of specific heats by the "method of mixture," of heat of combustion by the Berthelot or Mahler bomb, etc. It is reliable in ordinary practice within the limits of error imposed by the thermometry and by irregularity of conditions as to surroundings.

Following the brief statement of the "General Method" is that of a "special case" of that method, and of a "Modified Method." These are supplemented by a demonstration of the "Theory of the Methods," and a "Critique."

The procedure in the modified method is supposed to be new. Beyond that fact this paper claims the attention merely of those who desire a concise working statement of a method of cooling correction which has stood the test of practice.

General Method.

Procedure. — Start with the water of the calorimeter at any convenient temperature, e. g. about that of the air. If there is a water jacket around the calorimeter, let that be stirred thoroughly once for all, or, better, continuously. Record its temperature at the beginning and end of the measurements as a possibly useful check.

Let the water of the calorimeter be stirred thoroughly, continuously, and at a uniform rate. Record times and temperatures of the

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calorimeter each half-minute until the completion of the measurements (quarter-minute readings are sometimes preferable). After five or more minutes, at a noted time, drop in the hot substance, or start the calorimetric operation, whatever it may be, continuing the tempera-

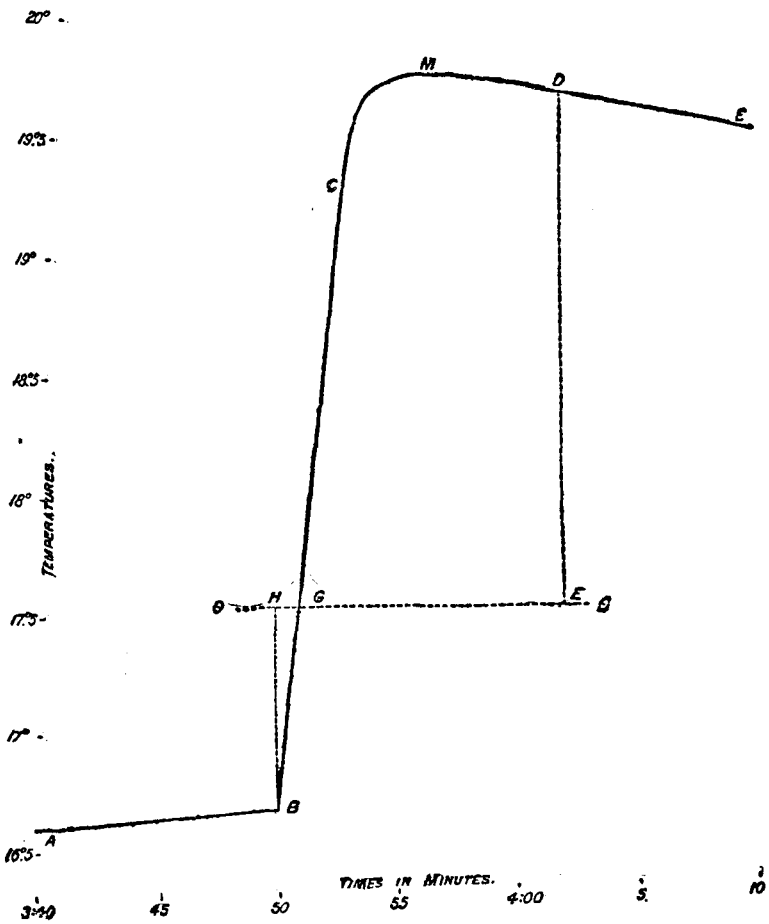

FIG. 1.

ture reading throughout the operation, and for at least five (better ten) minutes after its completion. The plot shows a typical set of observations.

A few readings may unavoidably be missed, where there is but one operator, viz. at the time B and in the steep part of $B\,C$; but

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these are unimportant, since the former can be obtained by prolonging the line through the data preceding the omission, and the steep part of $B\ C$ can be drawn in by judgment accurately enough because of the fact that it is of so short duration, and must be nearly straight.

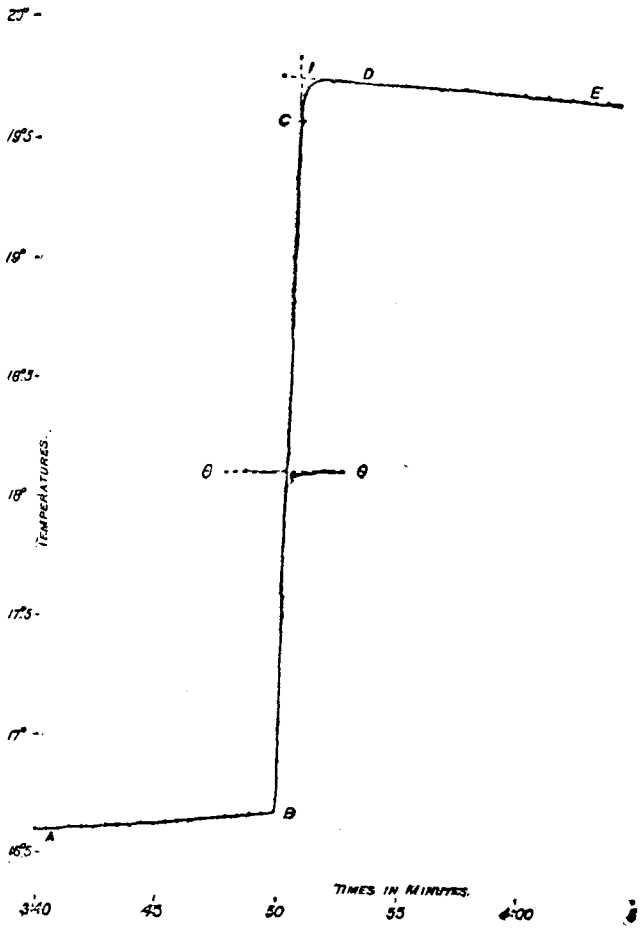

FIG. 2.

The Correction. — The significance of the terms given in this summary will appear on reading the "Theory of the Methods." From a plot, or from the data direct, find the initial rate r_1 and the temperature t_1 at the time m_1; also the final rate r_2 and temperature t_2 at m_2.

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From the plot or data compute the mean calorimeter temperature for the time interval $m_2 - m_1$ by the expression

$$T = \frac{1}{n-1}\left[\tfrac{1}{2}\,t_1 + b + c + \ldots + \tfrac{1}{2}\,t_2\right],$$

where n is the number of half-minute temperature readings t_1, b, c, $\ldots$, t_2. Compute also

$$a = \frac{r_1 - r_2}{t_2 - t_1}, \quad \text{and} \quad \theta = \frac{r_2}{a} + t_2, \quad \text{or} = \frac{r_1}{a} + t_1.$$

Then the corrected rise of temperature in the calorimeter will be

$$t_2 - t_1 + a\,(T - \theta)\,(m_2 - m_1),$$

or if the area method is adopted,

$$t_2 - t_1 + a\,A.$$

Special Case. — Where $B\,C$ is sensibly straight, and $C\,M$ (Fig. 1) is of short duration relatively to $B\,C$, then t_2 is to be found by prolonging $E\,D$ (Fig. 2) to its intersection in I with the vertical through C, the point where the operation ceased, or where $B\,C$ begins to deflect from a straight line. From C onward the exchange has been at the rate of $D\,E$; hence the ordinate of I may be taken as the temperature which would have been indicated had all the remaining heat been distributed throughout the calorimeter instantly when the operation ceased. This may be called t_2. The gain by exchange during the passage from B to C is obviously about $\frac{1}{2}\,(r_1 + r_2)\,(m_2 - m_1)$, where m_2 is the time corresponding to t_2. The corrected rise of temperature is then

$$t_2 - t_1 - \tfrac{1}{2}\,(r_1 + r_2)\,(m_2 - m_1).$$

Whether this special method is close enough can be determined for any series of measurements by solving a typical example both by it and by the general method.

Modified Method.

Procedure. — By computation from approximate or estimated values of the quantities involved, or from a preliminary trial, determine nearly what the rise of temperature in the calorimeter is to be and call this $\Delta\,t$. Start with the water of the jacket at, or a degree or two above, the temperature of the air of the room. In the calorimeter, start with the water $\Delta\,t^\circ$ *below that of the jacket*, or enough more than

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Δt to allow for unavoidable rise during preliminary manipulations, — in short, so that $t_1°$ shall be as nearly as may be $\Delta t°$ lower than $\theta°$. The object of this is to have t_2 so nearly θ that r_2 shall be nearly zero. On the plot of observations, Figure 1. this would cause $A\,B$ to incline upwards and $D\,E$ to become nearly horizontal.

Then proceed precisely as in the general method, both as to manipulation and computation.

Theory of the Methods.

A typical set of readings obtained under the general method, corrected for thermometric error, and plotted with times as abscissas and temperatures as ordinates, would lie along a line $A\,B\,C\,D\,E$, Figure 1. This curve should be convex upward all the way from C to D, there becoming straight. If any concavity shows itself between the maximum M and E, or if the straight line through the points between D and E cuts the curve anywhere between C and D, then the data should be rejected. For the inference, almost without exception, is that the stirring was insufficient to keep the thermometer down to the average calorimetric temperature. This may be due either to the bulb being badly located, so that it is unavoidably heated to excess, or merely to ineffective stirring. The difficulty should be removed, and the observation repeated.

The line consists of four portions, viz.: 1. The preliminary readings, A to B. 2. The readings during the operation, B to some indeterminate point C. 3. Readings C to D while the calorimeter and contents are becoming equalized in temperature. 4. Final readings after this equalization has become sensibly completed, and the calorimeter and contents are cooling, or heating, by exchange with their surroundings. In many cases, as in specific heat determinations, the second and third parts are one; that is, the operation *is* the equalization of temperature between the calorimeter and the substance introduced into it. In the case of a combustion and many other operations these two parts are to be distinguished.

The method is based upon Newton's law of cooling. Test observations have shown that this law holds with sufficient accuracy for both open and closed calorimeters, that is, within the uncertainty attributable to varying conditions of surroundings and to thermometric errors.

From the best representative straight line drawn through the observed points between A and B is deduced the initial rate of exchange,

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r_1 (positive for a rising, negative for a falling temperature), expressed in degrees per minute.

For the data between D and E, i. e. through the observations for the final few minutes, which will lie sensibly along a straight line, is deduced similarly the final rate r_2.

Let t_1 be the temperature at the point B, the beginning of the operation. Call this the initial temperature. Then r_1 is the exchange rate at t_1. Let m_1 be the corresponding time. Let t_2 be the temperature at the earliest minute or half-minute at which the line has become straight, that is, at which the fourth stage has been sensibly attained, e. g. the point D. Call this the final temperature of the calorimeter, and m_2 the corresponding time in minutes. Then r_2 will be the rate at t_2.

The average temperature of the calorimeter between m_1 and m_2 is next found as follows. Drawing through the points the best representative line $B\ C\ M\ D$, read off its ordinates at each half-minute (better each quarter-minute) from m_1 to m_2. Instead of a plot the corrected data may be used directly. Call these temperatures $a\ (=t_1)$, b, c, d, . . . , $n\ (=t_2)$, then the average temperature will be

$$T=\frac{1}{n-1}\left[\frac{a}{2}+b+c+\ldots+\frac{n}{2}\right]=\frac{1}{n-1}\left[\tfrac{1}{2}t_1+b+c+\ldots+\tfrac{1}{2}t_2\right].$$

This is, of course, the well known process. A slightly better one is to read off the temperature at the end of the first *quarter*-minute after m_1, then at intervals of a *half*-minute (viz. at $\frac{3}{4}$, $\frac{5}{4}$, etc.) up to m_2, which must therefore be selected at a point an even number of quarter-minutes from m_1, as there must be a quarter-minute interval at each end. The average of these also gives T.

By Newton's law of cooling, the rate of gain or loss of heat by a body through exchange with surroundings is directly proportional to the difference of temperature between the body and the surroundings. In calorimetry, provided that the heat capacity of the calorimeter and contents is not changed materially during the process (by the insertion or removal of substances), the rate of gain of temperature through exchange is proportional to the rate of gain of heat, so that the cooling correction may be applied directly to the temperature, instead of to the heat.

Under this condition, the rate of exchange of temperature when the calorimeter is at any temperature t will be

$$r=a\ (t-\theta),$$

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where θ = some constant temperature (representing that of the surroundings, which may not be uniform or known) and a = the rate per degree difference between θ and t.

The two quantities a and θ are unknown, but obviously can be computed from the two pairs of observed values, r_1, t_1, and r_2, t_2. For

$$r_1 = a\,(\theta - t_1); \qquad r_2 = a\,(\theta - t_2);$$

$$a = \frac{r_1 - r_2}{t_2 - t_1};$$

$$\theta = \frac{r_2}{a} + t_2, \quad \text{or} \quad \frac{r_1}{a} + t_1.$$

Both a and θ are next computed numerically from the data. θ is best found from the smaller value of r, for the reason that it influences the result most largely through its subsequent combination with values near that one.

The gain of temperature by exchange, then, in any short interval of time, Δ, during which the temperature is t, will be $a\,(\theta - t)\,\Delta$.

The rate of gain of temperature is $a\,(\theta - t)$, or $a\,\theta - a\,t$, so that, as θ is constant, r varies directly as t. Hence the average rate will be proportional to the average value of t, that is, to T, and will be $a\,\theta - a\,T$, or $a\,(\theta - T)$. The total gain will therefore be this quantity multiplied by the duration $(m_2 - m_1)$ of this average rate, or $a\,(\theta - T)\,(m_2 - m_1)$, and the exchange (or "cooling") correction will be this with reversed sign, viz.:

$$-a\,(\theta - T)\,(m_2 - m_1), \quad \text{or} \quad a\,(T - \theta)\,(m_2 - m_1).$$

The corrected rise of temperature of the calorimeter will then be

$$t_2 - t_1 + a\,(T - \theta)\,(m_2 - m_1).$$

Obviously $(T - \theta)\,(m_2 - m_1)$ is the area $H\,C\,O\,F\,H$ minus the area $B\,G\,H\,B$. This difference, A, in proper units, may therefore be measured on a plot by the planimeter or otherwise, and the corrected temperature rise will then be

$$t_2 - t_1 + a\,A.$$

Critique of the Methods.

Three assumptions, beyond that of Newton's law of cooling, are involved in the employment of this method, unless otherwise provided for in the computations into which the corrected rise of temperature is introduced. First, that the thermometer indicates the

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surface temperature of the calorimeter. Secondly, that the temperature distribution throughout the entire contents of the calorimeter is uniform both when r_2 and r_1 are taken, so that these are really rates of exchange with surroundings, and not resultants in which the desired rate is more or less modified by redistribution within the calorimeter. Thirdly, that the heat capacity of calorimeter and contents is the same both when r_1 and r_2 are taken.

Proper location of thermometer, efficient stirring, and the prevention of direct contact with the calorimeter of any hot or cold object within it, readily insure the fulfilment of the first with sufficient closeness.

Wherever the temperature of the calorimeter is varying, uniform distribution of temperature throughout its contents is obviously impossible if these are heterogeneous, especially where there is a large metallic mass surrounded by the water, as the bomb in the Berthelot or Mahler combustion apparatus. Such objects will necessarily lag more or less behind the water as the temperature of the latter falls or rises by external exchange. The effect of this is to falsify the apparent rate r_1 or r_2, and still further to vitiate the results through the usual assumption that all parts are at the same temperature. A form of cooling correction, taking this into account and applying to a certain class of cases, has been described by Professor Rowland, but the only method which could entirely eliminate the error would be to arrange the calorimetric process so that the rate of exchange should be sensibly zero or constant during the entire measurement. This means that the jacket temperature must be so controlled as to be always at the temperature of the calorimeter, or at a constant difference from it. While this at first sight appears wholly impracticable, and is so for most cases, I am disposed to think that it might be feasible and helpful in certain investigations, such as the study of the specific heat of water, and the mechanical equivalent of heat, using electrical methods of heating, combined with thermo-electric means of detecting and controlling the temperature difference between the calorimeter and jacket.

The "Modified Method" described above deals with this error in another way. It makes the final rate r_2 as nearly as possible zero, and hence secures the greatest possible constancy of temperature during the portion $C\,D\,E$ of the curve when the rate is about r_2. The advantages gained are as follows. The apparent rate r_2 is sensibly the true rate, since it will in general be much less than the rate of redistribution of heat amongst the contents of the calorimeter. This

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is of vital importance to freedom from constant or systematic error, because the duration of the rate r_2 is inevitably greater, often much greater, than of any other rate. If, as in the usual process, therefore, it is a large (often the largest) and the least accurately known rate, it is obviously productive of the most serious part of the error of the cooling correction. The modified method does not increase the lapse of time preceding the arrival of the final steady condition, D, which must in all methods, directly or indirectly, be the basis from which to deduce t_2. And as it does increase the percentage reliability of r_2, and reduces its amount, it diminishes the total amount of the correction, thus in a twofold way improving the result. The gain for operations of such a nature that the duration of $C\ D$ is several or many times that of $B\ C$ is large, being approximately in proportion to those durations. Into that category would fall many of the ordinary calorimetric processes, all those resembling the measurement of specific heats of liquids which cannot be mixed with that of the calorimeter, the use of the bomb for heats of combustion, and almost all processes involving the presence of considerable metallic or glass apparatus within the calorimeter. The method is of much less advantage where the duration of $C\ D$ is brief.

In certain cases there is a slight offsetting increase of error in r_1, namely, when the contents are heterogeneous when both r_1 and r_2 are taken. This occurs in the case of the bomb, but not that of the specific heats of liquids or solids. For then r_1 is a larger rate, and is inaccurate from the cause under consideration. Inasmuch, however, as this rate has during the operation $B\ C$ only a relatively short existence, and its error as affecting the value of a is divided by $(t_2 - t_1)$, the error introduced by it is small. It should be noted that if the calorimeter is used as a secondary apparatus, not as a primary or absolute one, the systematic parts of the above errors are further reduced. Thus, for instance, in using the bomb, the heat capacity of bomb, calorimeter, and entire contents may best be ascertained by burning in it a known mass of some pure substance of well determined heat of combustion (e. g. naphthalin), and computing backward from that heat to find the total capacity. This makes the apparatus a secondary one, dependent upon the assumed heat of combustion, but it is much safer than computing the capacity from the assumed specific heats and the masses of the component parts, or than measuring it by the addition of warm water in the well known manner.

Departure from the third assumption above named cannot be discussed in detail, since the effect varies widely with the change of vol-

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ume and exposed surface, as well as of heat capacity of the contents of the calorimeter in each case. Whether the change of capacity is sufficient to demand allowance can be usually determined by inspection of the case, and a special method of treatment provided. The usual effect is to make the apparent value of r_2 smaller relatively to r_1 than would correspond to Newton's law.

ROGERS LABORATORY OF PHYSICS,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
Boston, May, 1895.

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XIV.

CONTRIBUTIONS FROM THE CRYPTOGAMIC LABORATORY OF HARVARD UNIVERSITY.

XXXIV. — ON SOME POINTS IN THE DEVELOPMENT OF ÆCIDIA.

By Herbert Maule Richards.

Presented by T. W. Richards, November 13, 1895.

Very little has been published in the last twenty years regarding the development of the æcidium stage of the Uredineæ, and very little more is known than at the time when De Bary * wrote his text-book. Very recently Neumann † has given an account of the development of the æcidium, but his researches do not throw a great deal of light on the question. He is able to trace the origin of the basidia, or foot cells, as he calls them, only in a very general way, and as regards disputed points as to the formation of the peridium and the growth of the hymenium there is much to be said. Other authors have considered the question of the sexuality of the æcidium, but hardly any of them have taken it up from the developmental standpoint of the organ itself. Reference will be found to these papers in a general discussion at the end of this article.

In obtaining material for the study of the development of the æcidium it is necessary to consider several things. Not only must the material be plentiful, but the æcidium had best be a large one, and, above all, the tissues of the host of such a character as to allow of successful manipulation. For the latter purpose nothing could be better than an aquatic host, the tissues of which are usually loose, and the chlorophyll, at least in the more or less submerged portions, not so abundant as to interfere with a clear view of the hyphæ of the fungus. Nothing was found more favorable than an Æcidium on *Peltandra undulata*, which may be obtained in quantity in the neighborhood of

* Morphologie der Pilze, 1884.

† Ueber die Entwickl. der Aecidien, etc., Hedwigia, 1894, Heft 6.

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Boston during the spring. Most of the work to be described was done on this form, but Æcidia on *Houstonia cærulea*, *Ranunculus septentrionalis*, *Anemone nemorosa*, and *Sambucus Canadensis*, were also studied. *Peridermium elatinum* on *Abies balsamea*, and *Ræstelia lacerata* on the fruit of *Amelanchier Canadensis*, were also examined, and some particulars regarding the later stages of the æcidium seen in the other species were confirmed.

In all the work the methods of manipulation employed were the familiar ones. Sections were made both free-hand and with the microtome. With the microtome sections the material was stained either *in toto* or on the slide; Delafield's hæmatoxylin being found most favorable for the former, while for the latter and also for the hand sections eosin, Hofmann's blue, or Mayer's acid hæmalum was used. Lactic acid was usually employed instead of potash for distending and clearing the sections, because it does not disorganize and render so exceedingly transparent the tangled masses of hyphæ as does the latter. Most of the actual work of examination and almost all of the drawings were made while the sections were still in aqueous media, for any method of mounting soon renders the specimens so transparent that it is impossible to see the details. For final mounting, glycerine was usually preferred to balsam, although for the study of the nuclei specimens stained with hæmatoxylin and mounted in the latter were found the best. As is usual in the studying of structures of this sort, where certain differentiated portions must be disengaged from tangled masses of filaments, it was found that a tolerably thick section, properly dissected and macerated, was often more instructive than even a complete series of thinner ones.

Æcidium on Peltandra.

This form, which is the æcidium of *Uromyces Caladii*, being the one which was most thoroughly worked up, will be taken up first, to be followed by a discussion of the other forms named. The first material used for this examination was collected by Professor Thaxter, who kindly placed it at my disposal; quantities of the same æcidium have been collected by myself several times since, and the material killed in both picric and chromic acids. In selecting the portions of the plant for sectioning, petioles were usually taken, as they were easier to cut and also contained less chlorophyll than the leaves. By taking pieces of considerable length and cutting longitudinal sections the young æcidia could be traced with ease.

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For the earliest stages, pieces of tissue in which with a hand lens nothing but the spermogonia could be detected were taken. In sections of these, the youngest stages of what De Bary called "primordia" were seen, which consist of a large number of branching hyphæ, which are massed together and finally become compacted into an irregular sized ball. Even the youngest conditions may be distinguished from developing spermogonia, both by the fact that they are embedded more deeply in the leaf, and also because the hyphæ are more loosely arranged than in a spermogonium of equal size. After this massing together of the hyphæ to form the primordium has kept on for a certain time, changes are seen to take place. The hyphæ already septate become very much more so, and the small cells so formed begin to enlarge very much. The result is that a large part of the primordium now consists of a pseudo-parenchyma of cells of very irregular size and shape, and with walls of very variable thickness. Finally, the whole primordium changes to this pseudo-parenchyma with the exception of a weft of tightly woven hyphæ around the periphery, which merge at the base into a mass of somewhat more loosely compacted threads. A careful search was made in these young stages to determine if anything in the nature of a trichogyne could be found, but in all of the sections examined nothing to which the function of a trichogyne could be ascribed was seen. Occasional hyphæ were seen protruding out of the stomata, but they did not connect with any of the primordia, and showed no evidence of any specialization.

During the formation of the pseudo-parenchyma, the young æcidium increases very much in size, and consequently displaces the cells of the host plant. The primordium, starting in a large intercellular cavity, fills it, and then the hyphæ, pushing out, soon surround the neighboring cells, and often cut them off from their fellows. Such isolated cells are usually completely broken down by the hyphæ, and apparently absorbed. In this case practically no distortion accompanies the growth of the hyphæ or æcidia.

Earlier than the formation of the pseudo-parenchyma no sign is seen of the hymenium, nor can the hyphæ which are to form it be distinguished. At about this stage, however, there arises at the base of the primordium a definitely differentiated hypha, which may in respect to its further development be called the fertile or sporogenic hypha. It is to be distinguished from the ordinary sterile hyphæ which surround it by its highly granular and somewhat more refractive contents. It absorbs aniline stains slowly, but to a great amount,

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finally becoming much more deeply colored than the surrounding threads. It is not, however, very easy to demonstrate, and many sections must be examined before obtaining the fortunate ones which will show it.

At first the fertile hypha presents no very characteristic form, but as time goes on it becomes twisted sometimes almost spirally (Fig. 1). Although usually simple in the beginning, later it may fork, or even branch several times. This fertile hypha may be traced down in among the mass of threads at the base of the primordium, and there is nothing to indicate that it originates from any specialized organ, but simply from the undifferentiated mycelium. The subsequent development of it which leads to the formation of the hymenium is subject to some variation. In the smaller æcidia the fertile hypha simply begins to bud out at the tip into short projections which are young basidia (Fig. 2), but in the larger æcidia it may branch so that the hymenium may arise from several points (Fig. 3). In this species the contents of the fertile hypha very soon pass into the buds of the young hymenium, leaving it empty and quite indistinguishable from the surrounding hyphæ. Following the development of one of the smaller Æcidia, it is seen that the buds rapidly increase in number and assume a more definite position. The larger older ones are usually in the centre of the cluster, and the young buds are formed around the periphery (Fig. 4). The young basidia are cut off from the central mass as fast as they are formed, and after enlarging somewhat show other cross septa, which are the first indications of what may be called the spore mother cells. To make room for the developing hymenium, the pseudo-parenchyma usually splits at this juncture. A rift is formed in the centre of the primordium, and, the cells around it collapsing, there is left a large cavity into which the young basidia push up (Fig. 2). As the basidia increase, they finally compress the pseudo-parenchyma, until in the mature æcidium it is seen only as a narrow covering outside of the peridium, made up of the collapsed and almost disorganized cells which formerly filled the whole primordium.

The development of the hymenium in the larger æcidia is essentially the same, except that in place of a single compacted mass of basidia they arise over a somewhat larger area or from several distinct points (Fig. 3). Soon, however, the basidia form a solid mass, and, although there is a certain amount of intercalary formation, most of the growth of new basidia takes place around the periphery of the hymenium.

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The septation of the basidia which started in the older ones is continued by the younger ones near the periphery, and the next definite change that is to be noted is the beginning of the peridium. The formation of the peridium commences by the differentiation of the terminal cells cut off from the older basidia. Their walls become definitely thicker and their contents very vacuolate, presenting quite a distinct difference from the spore mother cells below (Fig. 3). As the other young spore chains push up, their terminal cells also become similarly altered and the formation of the peridium progresses rapidly from the centre outwards. The peridial cells so formed increase more rapidly in size than the spores below, and owing to this and the interpolation of new basidia, which grow up from the base, their connection with the chains of cells from which they originated is often lost. Sometimes, however, this connection is retained quite clearly even when the æcidium is well along in its development, due perhaps to the fact that in such cases the young basidia have grown up more nearly simultaneously than usual and that there has been no intercalary formation of basidia. At times the enlargement of the peridial cells is more rapid than need be to cover the hymenium as it enlarges, in which cases they may be pushed out of place so as to give the appearance of a double layer of cells.

This metamorphosis of the terminal cells continues to the very margin of the hymenium, and there the same modification affects the whole peripheral row of spore chains, so that the æcidium is now completely incased in a covering of modified spores which may be called the peridium. This last point is shown better in other æcidia than the one now under discussion, and will be referred to later. Nothing was seen that would lead one to suppose that the peridium originated around the periphery and grows up until it meets in the centre, nor did it appear that it is derived in any way from the pseudo-parenchyma layer, for the line of demarcation between this and the peridium is always apparent (Fig. 3).

Concerning the formation of the spores there is not much that is new to be said. They are cut off basipetally from the basidia or foot cells, and the cells thus formed are being constantly pushed up by the formation of new ones below. The upper row forms, as has already been described, the peridium; from the others the spores are produced. In these cells may be seen a double nucleus, or rather two nuclei almost always in close proximity to each other (Fig. 5, *a*). These have already been described by Rosen,* and also by Dangeard, but as

* Cohn's Beitrage, VI.

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my own observations as to the fate of these nuclei do not entirely correspond with Rosen's view, there remains something to be said about them. The cells which are first cut off from the basidia are not the spores themselves, for from their proximal end is always cut off a small usually wedge-shaped cell (Fig. 6, *a*, *b*) the interstitial cell of De Bary. The larger upper cell becomes the spore, the small lower one eventually disappearing.

In the basidia there are always two and often more nuclei. When a spore mother cell is about to be cut off one of these migrates to the tip and there divides, a septum is soon formed below it, and the spore mother cell is formed. Rosen states that when the interstitial cell is about to be cut off, each of these twin nuclei divides, and from the four daughter nuclei so formed two migrate to the lower end of the cell, where they are cut off, and the other two remain in the spore proper. In my own observations in by far the majority of cases the nuclei separated without dividing, and were separated as single nuclei, one in the spore and one in the interstitial cell (Fig. 6, *a*). The nucleus in the spore always divided at least once, — in a considerable number of cases, indeed, three nuclei were seen in the ripe spores (Fig. 5, *b*, *c*), — while the nucleus in the interstitial cell sometimes divided, but quite as often remained single, as long as the interstitial cell persisted. As the spore ripens, the wall thickens and becomes rough, the interstitial cell disappears, and the spore may be said to be mature. The double nucleus remains quite distinct in the spore to the oldest stages.

In speaking of the double nuclei in the spore it should be mentioned that they are found in all of the other parts of the æcidia, in the hyphæ, the pseudo-parenchyma, and the peridium. This ubiquity tends to deprive them of so great a significance as some authors have placed upon them.

It is not necessary to follow the development of the æcidium any further, the final rupturing of the peridium, etc. having been often described in other forms.

Æcidium on Houstonia cærulea.

Most of the material used for the examination of this species was collected by Professor Thaxter, who kindly allowed me free use of it. A small amount collected by myself at Sharon, Mass., was killed in picric acid, and was valuable for some of the younger stages. This æcidium is found both on the leaves and corolla of its host. The

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leaves, owing to their comparatively loose structure, and to the fact that the chlorophyll was mainly disorganized by the fungus, proved the best for use.

In the mature æcidium nothing of note is to be observed which differs from the æcidium already described. The layers outside of the hymenium are better developed and the peridial cells and spores smaller than in the æcidium on Peltandra. The whole æcidium is more compact. The intercalary cells are very prominent and in them, perhaps on account of their large size the double nuclei are usually easily seen.

The fertile hypha appears at about the same stage as noted before. When it is traced back it is seen to merge into the rest of the mycelium, and at first can only be told by its more granular and refractive contents. Perhaps the best case observed was seen in Figure 7, where at the base of a young primordium is seen a very much twisted highly granular hypha which has already sent out a branch from which the hymenium will develop, as in Figure 8. In the somewhat older æcidia the young basidia may be seen to radiate very distinctly from a common centre, which marks the position presumably of the end of the fertile hypha (Fig. 9).

The subsequent development of the spores and peridium accords well with that already described in the previous case, with the exception of the fact that the pseudo-parenchyma does not split as in the æcidium on Peltandra, but is gradually pushed aside as the hymenium develops.

Æcidium on Ranunculus septentrionalis.

On the lower sides of the leaves and on the petioles of Ranunculus this species of æcidium may be found occurring in clusters, with the older æcidia in the centre and the younger around them. A considerable quantity of the material was collected by myself in the vicinity of Cambridge in the spring of 1894.

The mature æcidia present no great peculiarities, with the exception of a very considerable variability in the size of the peridial cells. Ordinarily they are large, much larger than the spores, but occasionally specimens are found with very much smaller cells. In such cases, it is quite easy to trace their connection with the spore chains below: they differ but little from the spores in size, but have the characteristic walls of peridial cells. It is possible that this condition may be explained by a delay in the formation of the peridium in such cases. The hymenium having attained its full size, there was not the same

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necessity for the rapid growth of the peridium to cover it. Interstitial cells are present, and do not show anything unusual. The usual double nuclei were easily demonstrated in all the various parts of the æcidium.

This æcidium proved more favorable than some to demonstrate the connection of the basidia with the fertile hyphæ. In one fortunate macerated preparation a somewhat tortuous hypha was seen, from which branches arose that terminated directly in the basidia (Fig. 11). The character of the leaf was not favorable for the study of the younger stages, as the compacted condition of the tissue and the presence of much chlorophyll obscured the young primordia. Nevertheless, several interesting stages were seen that are worthy of note since they help to substantiate the observations made on the other æcidia. In Figure 10 a section of a young æcidium is shown where the fertile hypha has pushed its way into the already fully developed pseudo-parenchyma. From the fertile hypha, in which many nuclei could be made out, there have arisen the first buds from which eventually the basidia and spores will be formed. Unfortunately this otherwise excellent section was marred by the fact that the hypha was cut off only a short distance below the place where it had begun to bud out. Its connection with the hypha below, as indicated by the dotted lines, was only inferred by the similarity of their contents and general appearance. At this early stage no septa could be seen that cut off the buds from the parent hypha. Other stages of a similar sort, some younger and others older, were found, but none showed as clearly as the one just described. A very much younger condition, where the fertile hypha is but a simple thread with a rounded end and rich in granular contents, was perhaps the earliest condition observed. In some of the larger æcidia, which however never approached the size often attained by the æcidium on Peltandra, ther were apparently more than one point of origin for the basidia.

Æcidium on Anemone.

This form, which is *Æcidium punctatum* Pers., is in many respects unfavorable for examination, but, as it was apparent that it presented some variation from the type already described, some work was undertaken on it. The æcidia do not occur in clusters, as in some other cases, but are more or less scattered over the under side of the leaf; but they have a certain advantage over other æcidia in that the spermogonia being so very superficial there is never any danger of confusing the young stages of these two organs.

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The basidia are comparatively short, and the layer below them, which may be called the sub-hymenial layer, is much more closely compacted than in any of the forms previously described in this paper. It is also noticeable that the base of the hymenium, which in other cases, at least in the younger stages, is often somewhat rounded, is here practically flat, since the basidia almost all terminate on the same level. The primordium progresses in its development without much variation from the general rule, except that the amount of pseudo-parenchymatic tissue is relatively smaller, and the surrounding weft of hyphæ relatively larger than in the three æcidia already described. It was evident from the appearance of the young hymenium, in which the basidia develop much more nearly simultaneously than in the cases already noted, that there was some variation in the development of this form from the types previously examined.

Below the young basidia in the sub-hymenial layer there could be distinguished fertile hyphæ, from which the basidia are budded out, and sterile hyphæ that wound in among them (Fig. 12). The former could be separated from the latter on account of their power of staining deeply. This layer of sporogenous hyphæ which underlies the pseudo-parenchyma gives rise to the basidia more nearly at the same time than they arise, for instance, in *Æcidium Caladii*, although even here it is apparent that the younger basidia are the ones nearer the periphery of the hymenium. The fertile hyphæ arise from the branching of hyphæ that make their way up from below, and apparently the sporogenous layer may arise from more than one of such hyphæ. This course of development much more nearly corresponds to that given by Neumann * than any of the others do, but is not exactly as he describes it in the æcidia he investigated.

It was in this species especially that hyphæ were seen protruding through the stoma, but examination failed to show any connection of such hyphæ with the primordia, and it was probably due more to the very great crowding of the mycelium in the leaf than to any other cause. The subsequent development of the spores and peridium failed to reveal any noteworthy peculiarities. This æcidium is especially interesting as showing a variation from others in the matter of its development, but a discussion of this point will be reserved until a few words have been said about some other æcidia which afforded interesting facts, especially regarding the formation of the peridium.

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* *Loc. cit.*.

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Aecidium on Sambucus.

In this æcidium there is a considerable amount of distortion of the tissues of the host, but at present only the æcidium itself will be considered. It did not afford a very good chance for studying the younger stages, but, as nearly as could be made out the development corresponds more nearly to that of the æcidium on Ranunculus than to any other.

The peridium begins in the usual way from the metamorphosis of the terminal cells in the older spore chains, and spreads over the top of the hymenium, as already described. The fact that the side walls of the peridium correspond to the outer row of spore chains is excellently shown in this species. The peridial cells, which become smaller and thinner walled as they approach the base of the hymenium, are seen finally to merge into a foot cell which exactly resembles the other basidia. In the youngest peridial cells even the interstitial cells were observed, although De Bary in his text-book says that they are not present in the peridium (Fig. 13). Very soon, of course, owing to the enlarging of the peridial cells and to the thickening of their walls, the interstitial cells disappear sooner than they do between the spores.

Passing to the Æcidium known as *Peridermium elatinum*, we find an interesting variation in the formation of the primordium. What may be properly called the primordium in this case is but poorly developed, consisting of simply a mass of loosely arranged pseudo-parenchyma of rather large cells, and with none, or practically none, of the hyphal weft about them. It is not improbable that this form might prove a very excellent one for studying the young stages of the hymenium, and it is greatly to be regretted that the material at hand was too advanced for that purpose. The formation of the peridium, however, showed admirably. In Figure 14 a young æcidium is shown, in which two peridial cells have just begun their differentiation from the spore chains. The mature æcidium, aside from the necessary reduction of the mass of collapsed pseudo-parenchyma outside of the peridium, showed no great peculiarities.

The last æcidium to be considered is Rœstelia. It was hoped that, owing to the long period of formation that the Rœsteliæ undergo before they emerge through the tissues of their hosts, it might be coupled with some longer preparatory growth of the æcidium itself. Such, however, did not prove to be the case, for in all of the species examined, although the origin of the Rœstelia was very deep in the tissues of the host, and consequently it was a long time in

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breaking through, the spores and peridium began to form as early as in the other æcidia. The subsequent development was simply a multiplication of the spores and peridial cells. In the species chiefly examined, *Ræstelia lacerata* on *Amelanchier Canadensis*, there were however some facts made out that should be mentioned.

The mass of pseudo-parenchyma in the primordium is elongated vertically, and appears still to keep on forming, while the hymenium is developing, until it almost reaches the surface of the tissue in which it lies. Although excellent young material was obtained, it was impossible, owing to the very compact and obscure nature of the primordium and the very small size of the hyphæ, to make anything out of the youngest stages even by all the various methods tried. The young basidia are very narrow, and those which form the peridium swell abruptly into the peridial cells, which at first, though large, are very thin-walled. The intercalary production of basidia is more marked here than in any æcidium previously examined, and owing to this the connection of the peridial cells with the spore chains is rapidly lost. The cells of the peridium, which are at first about the normal shape, lengthen very much, and become of the elongate almost rhomboidal shape found in the mature æcidium.

General Discussion of the Æcidium Stage.

In comparing the results of the foregoing observations with the accounts of the development of the æcidium already published certain differences of considerable importance will be noticed. As regards the formation of a primordium with a mass of pseudo-parenchymatic cells in the centre, there appears to be a general unanimity of opinion, although Neumann * figures the formation of the hymenium at a much earlier stage than seems to be the case in the æcidia described here or in those mentioned in previous accounts. In Plate XVI. Fig. 3 of his paper he shows very definite indications of a hymenium before the appearance of the compact pseudo-parenchyma. The same is true of his figure of the æcidium on *Ficaria ranunculoides*, but if one may judge from the drawing of the form on *Euphorbia Cyparissias*, the condition is more nearly as I have seen it myself, where there is a definite pseudo-parenchyma before the formation of the young basidia. Concerning the formation of the sporogenous hyphæ, there seems to be but little better knowledge in the pub-

* *Loc. cit.*

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lished accounts than there was at the time De Bary wrote his text-book. All that De Bary says is, that after the formation of the primordium with its pseudo parenchyma, "the hymenium now makes its appearance at the base of the æcidium." etc.* He also leaves in doubt the question of the manner in which the hymenium increases in area, whether it is by the peripheral or intercalary formation of new basidia. Plowright † throws no light on either question, leaving them just as De Bary has. There is really nothing which deals with the question further, until we come to Neumann's paper already mentioned. Even here the matter of the origin of the basidia is passed over somewhat vaguely, being referred to as being cut off from the hyphæ. In the question of the enlargement of the hymenial surface, it will be seen that his conclusion and the one put forward in this paper do not entirely coincide. He expresses the opinion that all of the basidia arise practically simultaneously, and that one cannot speak of any after-growth of new ones. This is certainly not the condition found in the æcidium of Peltandra, or of forms like it, although in the æcidium on Anemone something more nearly approaching it is seen. The opinion of De Bary that the hymenium usually starts from a comparatively small centre is borne out by my own observations. The opinion expressed here, which seems to have basis in the facts observed, is that the formation of new basidia, while mainly peripheral, is also to some extent intercalary, and that in most æcidia they are not formed simultaneously.

As regards the origin of the basidia Neumann adds but little, and there have been practically no suggestions in this direction except a very brief account by Massee ‡ of the occurrence of an oögonium which after fertilization by an antheridium, after the manner of the Peronosporeæ, grew out into the basidia. It is unnecessary to do more than refer to this publication, and to add that, so far as the observations recorded here go, nothing of such a nature was discovered. There are, however, certain definite fertile hyphæ which rise from the mycelium and push their way into the primordium. It has also been seen that these hyphæ are often twisted, even spirally bent, suggesting possibly the "Woronin's hyphæ" seen in the development of certain Pyrenomycetes. From these hyphæ are given off buds or branches

* De Bary, Comp. Morph. of the Fungi and Mycetogoa, Garnsey and Balfour's trans., page 274.

† British Uredineæ and Ustilagineæ, 1889, p. 22.

‡ Annals of Botany, 1889.

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which give rise to the basidia. At this point there is apparently some difference in the development of different species, and even in the æcidia of the same species. In the æcidia on Peltandra and Houstonia, at least among the smaller ones, the basidia arise with but little branching on the part of the fertile hypha, while in the form described on Ranunculus the fertile hypha seems to branch to some extent, and in the æcidium on Anemone it forms apparently an extended growth before giving rise to the hymenium. It is probable that in some cases, particularly in the larger æcidia, more than one fertile hypha takes part in the formation of the hymenium.

In the formation of the spores, there is first formed what may be called the spore mother cell, from which by division is formed the spore itself and the small interstitial cell, in the manner previously described. Plowright * speaks of the spores as being formed *in* a mother cell, and that by subsequent growth and thickening of the walls the spore and the mother cell fuse together. Such, however, can hardly be considered the state of affairs, for the intercalary cell is plainly cut off in the manner described by Rosen and also given in this paper.

Regarding the peridium, the view advanced here is probably more different from the generally accepted idea than any other particular mentioned in this paper. Almost everywhere one finds the statement that the peridium originates along the sides and "arches over" the hymenium. De Bary has said that the cells of the peridium do not possess intercalary cells, but this is hardly the case in the æcidium herein described on Sambucus, although in other cases the thickening of the wall might begin before it was time for the intercalary cell to be formed, in which case its production might be interrupted. It might be objected that the union of the terminal cells with the peripheral spore chains to form the peridium is hard to account for, but when one considers the condition of affairs in the young æcidium it is not so difficult to understand. The walls of the young peridial cells are very delicate, and, being under a relatively considerable pressure, are literally forced together. It is true that in their subsequent development the peridial cells on the side increase mainly in length, while the peridial cells on the top of the æcidium increase in all directions; but that is hardly an unsurmountable objection. It may be that it is the pressure under which the cells of the peridium are formed which induces the excessive thickening of the wall.

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* *Loc. cit.*, p. 22.

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It has been the view of some writers that the peridium is the result of a development from a circle of paraphyses, and the condition of the æcidium of Phragmidium is cited in support of this view. But, as De Bary * has said, the paraphysal envelope of this æcidium is not well understood, and no light has been thrown on this matter since he wrote regarding it. Whatever may be the condition in this æcidium, however, it is safe to say that the peridium of the ordinary æcidium is the result of a metamorphosis of the outer layer of spores.

As to what interpretation is to be placed upon the æcidium, and what place it occupies in the life history of the Uredineæ, so much has been said, and so little comparatively is known, that a re-discussion cannot bring out much that is new. What has been described in this paper, although perhaps not of the most positive nature, certainly rather supports than contradicts the view held by De Bary. In the æcidia here investigated, it would seem that the æcidium is not to be regarded at the present time as the result of a sexual process, but that it has a definite spore-bearing hypha, possibly corresponding to the archicarp.

Some of the more recent writers in text-books have entirely disregarded De Bary's view, and speak of the Uredineæ as forms of fungi with three chlamydosporic stages, in some cases comparing the chains of æcidiospores and their interstitial cells with the chlamydospores found in Chlamydomucor. This seems to carry it to somewhat of an extreme, for one certainly does not associate with chlamydosporic conditions such relatively complicated sporocarps as are found in the Uredineæ.

Vuillemin † has recently published an account of the æcidiospores, in which he maintains to have found the equivalent of a sexual stage in the union of the double nuclei found in these spores. The question of the sexuality of such a process, should it occur, can hardly be discussed here, for the idea itself naturally suggests its own objections, particularly in the light of the ubiquity of the double nuclei throughout the Uredineæ. It is interesting to note in this connection a fact already recorded, that triple nuclei have been not infrequently seen.

To sum the whole question up, it seems to the writer that the view expressed on this question by De Bary, where he likens the æcidium to the sporocarp, has more basis in fact than any other theory, but that at the present time there is no sexuality in the process of the forma-

* *Loc. cit.*, p. 246.

† Comptes Rendus, 1893, Vol. CXVI. p. 1464.

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tion of this sporocarp. Hartig* has said that it is probable that the æcidium is the result of a preceding sexual act, and is therefore a true sporocarp, like the perithecium and apothecium of the Ascomycetes. This is stating the case strongly, but even if the æcidium is not the result of a sexual act, it does not preclude the comparison with the sporocarp, for it has been abundantly shown that the sexuality in the formation of the latter is often much reduced among many fungi, the Ascomycetes in particular.

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* Diseases of Trees, Trans. Somerville and Ward, p. 153.

CRYPTOGAMIC LABORATORY, HARVARD UNIVERSITY,
May, 1895.

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EXPLANATION OF PLATE.

Æcidium of Uromyces Caladii on Peltandra.

1. Section of primordium showing fertile hypha. × 320.
2. Older stage, where the fertile hypha has begun to bud. × 320.
3. Young stage of a large æcidium showing several points of origin of hymenium. The peridium has begun to form. × 320. *a*. Showing the formation of the peridium at a somewhat later stage. × 320.
4. More advanced stage of same. The pseudo-parenchyma has ruptured. × 320.
5. *a*. Single ripe spore showing double nucleus. *b*. Spore with three nuclei. × 1250.
6. Young spore just cut off from the basidium showing nuclei. *b*. Spore; older, but not yet mature. × 1250.

Æcidium on Houstonia cærulea.

7. Section of primordium with fertile hypha. × 320.
8. Older stage, showing connection of fertile hypha with young basidia. Not quite median although showing the fertile hypha. × 320.
9. Section of young æcidium, showing a somewhat older hymenium. × 320.

Æcidium on Ranunculus.

10. Section of primordium with fertile hypha already budding. × 320.
11. Section of an almost mature æcidium, in which the connection of the fertile hypha with some of the basidia is plainly shown. × 320.
12. Young basidia from æcidium on Anemone (*Æcidium punctatum*). The sterile hyphæ, the contents of which are not so granular, show among the fertile ones. × 560.
13. Margin of a section of æcidium on Sambucus, showing origin of the peridium. × 560.
14. Young æcidium of *Peridermium elatinum*. × 320.

All the drawings were made with the aid of an Abbé camera and reduced about one third in reproducing. Figures 3, 3*a*, 4, 5, 6, 7, 9, and 14 were drawn from microtome sections, the rest from hand sections. All were treated with lactic acid, and stained before drawing.

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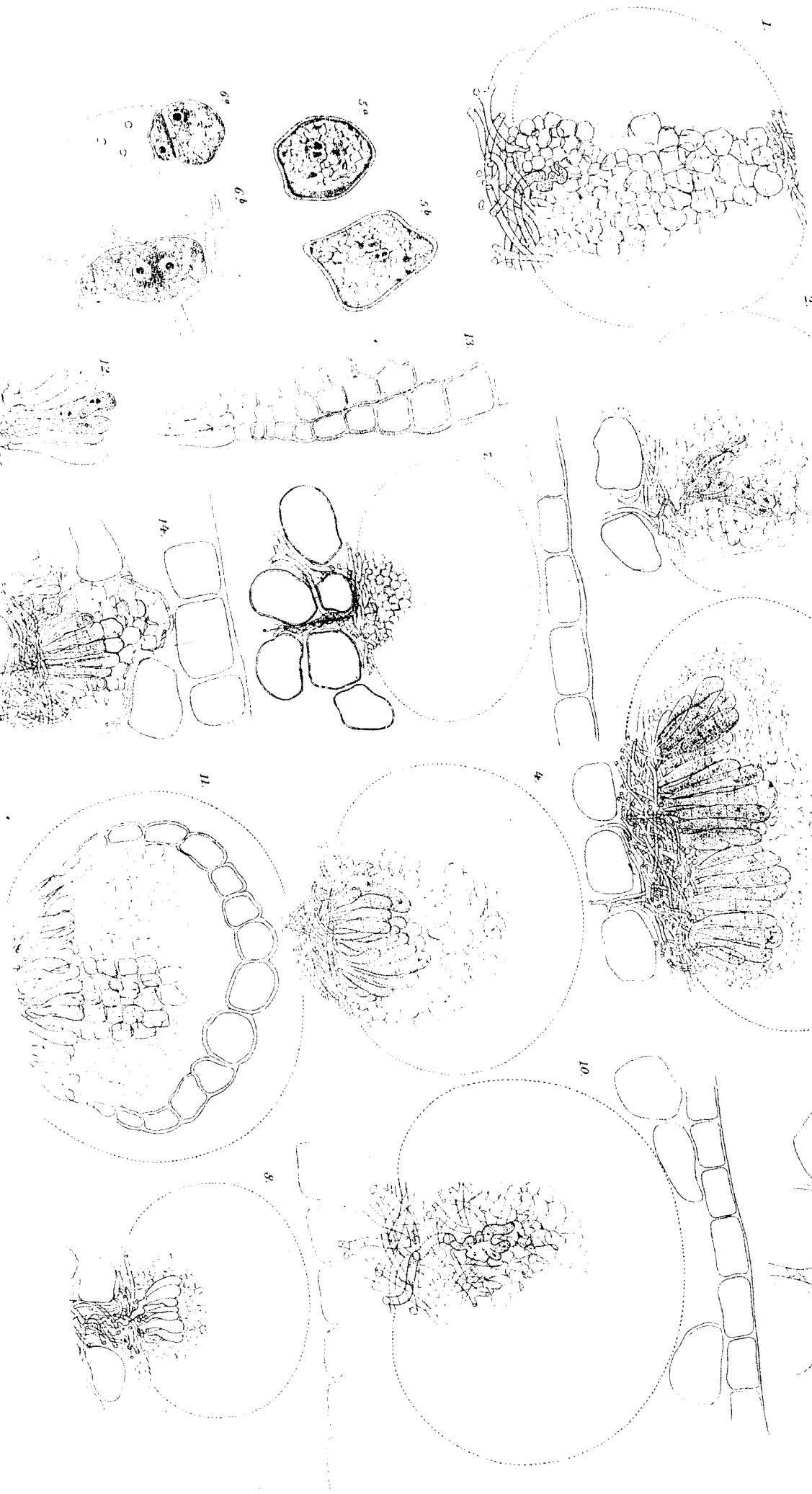

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XV.

ON THE THERMAL CONDUCTIVITY OF MILD STEEL.

BY EDWIN H. HALL.

Presented January 8, 1896.

SOME years ago,* the author gave an account of certain experiments which he had made, by the method of Forbes, upon the thermal conductivity of cast iron and cast nickel, and stated that he hoped "soon to make trial of a method for estimating thermal conductivities somewhat different from any heretofore used." This method has now been tested, and it appears to be a good one, although certain changes in the apparatus used, and presently to be described, might be made with advantage.

It is well known that early experiments upon thermal conductivity were made with thin plates or sheets of metal. The results obtained were absurdly erroneous, owing mainly to the difficulty of determining accurately the difference in temperature of the two faces of the plates. Later the method was by various devices made to give better results, but none satisfactory, and for a long time it has been discarded, replaced generally by the method of Forbes, steady flow of heat in a long bar exposed to the air, or that of Angström, waves of heat sent along the bar at regular intervals. None of the methods have been very simple, or easy of application, and the results obtained in the case of the metal most studied, iron, have been as various as the difficulty of the investigation would lead one to expect.

Every one who has engaged in the experimental study of heat conduction, or has examined the curiously indirect methods employed in this study, must have regretted the apparent impossibility of using successfully the old method of thin plates. About four years ago, it occurred to the author that one might determine the difference in temperature of the two faces of a thin plate by making these faces

* These Proceedings, Vol. XXVII. p. 262, 1892.

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the junctions of a thermo-electric element. Suppose, for example, that a plate of iron is coated on its two broad faces with a layer of copper, and that copper wires lead from these copper sheets to a galvanometer. If one copper side is exposed to water at $t°$, and the other copper side to water at $t'°$, heat will flow through the whole plate, and the difference in temperature of the two surfaces where the iron joins the copper sheets will give rise to a thermo-electric current, which may be made to give an accurate measure of the difference of temperature of the two faces of the iron plate. No attempt need be made to determine the difference in temperature of the outer surfaces of the copper sheets. This is an outline of the most distinctive feature of the method now to be described. The chief obstacle has been, and still is, the difficulty of getting a sufficiently even temperature over the whole of each surface.

Figure 1 shows with tolerable accuracy a vertical section through the conducting disk and the apparatus most closely connected with it, the parts being represented at one third their actual size. Certain unessential changes have been made in the drawing, in order to illustrate as many features as possible in this one figure.

S is the conducting disk of iron, or, rather, "open-hearth" boiler-plate steel. The following information concerning its quality and composition was furnished by Mr. Parker, of Parker, Field, and Mitchell, Cambridgeport, who made the disk: —

Tensile strength	62,300 lbs. per sq. in.
Elastic limit	34,800 " "
Phosphorus	.0035.
Carbon	.001.

The analysis was made by the Central Iron and Steel Works of Harrisburg. The metal is very soft and tough, as the composition would indicate.

The mean thickness of the disk, which was carefully measured at many points, is 0.295 cm., the smallest thickness found being 0.290 cm., and the largest, 0.299 cm. The diameter of the disk is 9.80 cm.

The parts c and c' are the coatings of copper deposited electrolytically upon the steel. The author hesitated at first to apply copper in this way, fearing that galvanoplastic copper might be seriously different in thermo-electric quality from ordinary copper wire, which must be attached to the coatings; but all his own experience and that of Professor B. O. Peirce, who has had occasion to

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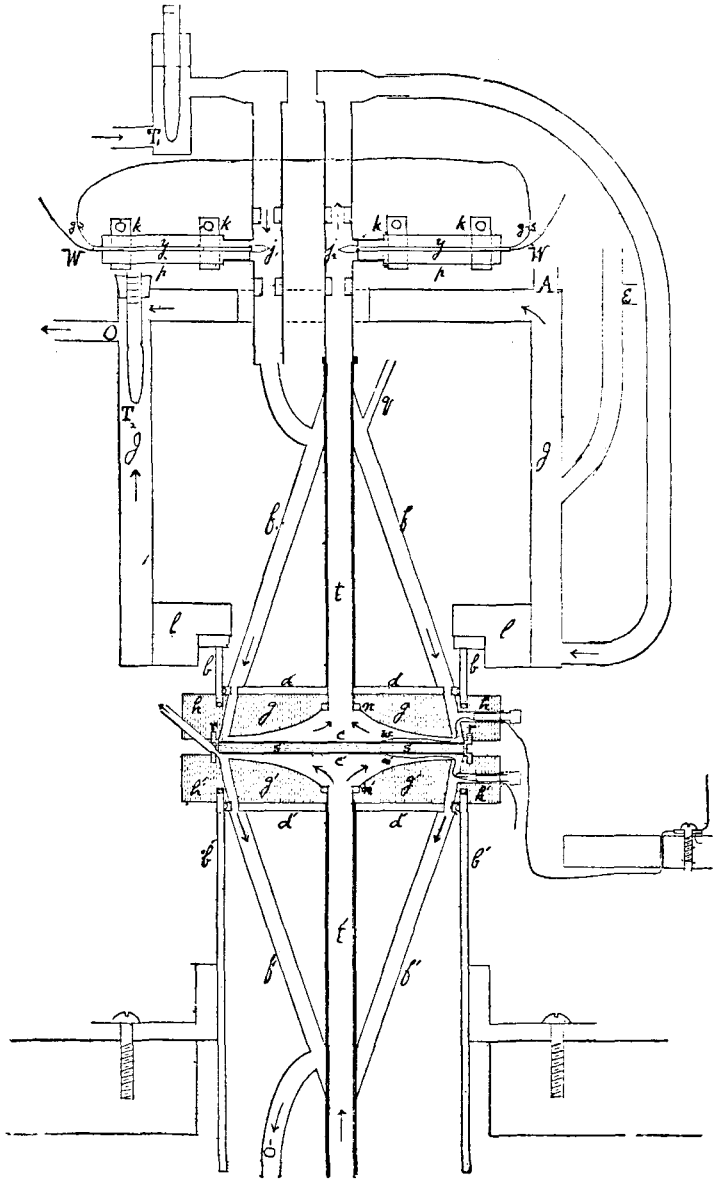

FIG. 1.

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investigate the same matter recently, go to show that this apprehension was groundless, that different specimens of copper wire now purchased in the American market differ very little among themselves in thermo-electric quality, and differ very little from galvanoplastic copper.

The ordinary method of depositing copper, from a sulphate solution, is not immediately available for a steel plate, because the solution attacks steel. On the other hand, the method which uses a cyanide solution is comparatively slow, and requires much time for a thick coating. Accordingly, the disk here used was subjected to the depositing current in a cyanide solution for a sufficient time to cover the surface completely, and was then transferred to a sulphate solution, where the process was continued for many hours, until the coating was about 0.05 cm. thick on each side of the disk.

The letters *r r* in the Figure mark a ring of steel, similar in quality to the disk. It was turned a bit too small to receive the disk when both were at the same temperature. The ring was then heated, and the disk, smeared on the edge with a pitchy cement, was slipped into it. The contraction of the ring in cooling made a joint so tight that under severe tests no leakage through it has been detected.

The parts *h h* and *h′h′* are rings of hard rubber. These rings do not extend quite to the copper coatings of the disk, but leave a line of the steel ring *r r*, about 0.07 cm. wide exposed, above and below these coatings. These exposed edges have caused trouble through rusting, under the action of the water flowing through the apparatus. No varnish protects them effectually. In future experiments care will be taken to have no iron or steel similarly exposed.

The parts *b b* and *b′b′* are hollow brass cylinders about 10 cm. in external diameter, fitting into grooves in the hard rubber rings *h h* and *h′h′* respectively, a small rubber tube at the bottom of each groove being used to make, under pressure, a water-tight packing of the joint. At first these brass rings fitted directly into the ring *r r*, the rings *h h* and *h′h′* not being used. But it soon appeared that heat, carried to or from the ring *r r* by the rings *b b* and *b′b′*, each of which in the first arrangement exposed a broad surface to the water, made the difference in temperature between the top and bottom of the disk much greater near the edge than elsewhere. For it is to be noted that the temperature difference between top and bottom of the disk was in most parts only a small fraction, perhaps 5%, of the maximum temperature difference between the water above and the water below the disk.

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The parts $d\,d$ and $d'd'$ are disks of brass, the edges of which press upon the rings $h\,h$ and $h'h'$. These disks are perforated near the edge by numerous holes for flow of water. The disks are packed water-tight, or nearly so, in the brass rings $b\,b$ and $b'b'$, small rubber tubes being used in the joints.

The parts $g\,g$ and $g'g'$ are blocks of hard rubber secured by the nuts n and n' to the brass tubes t and t'. The object of these blocks is to guide the flow of the water across the surfaces of the disk in order to make the temperature over each surface as nearly as possible everywhere the same.

The block $g'g'$ is not fastened to the disk $d'd'$ upon which it rests, but is carried by the tube t' in such a way that when t' is rotated $g'g'$ turns with it. It was the practice at certain stages of the work to rotate t' briskly back and forth through a number of degrees, in order to facilitate the escape of air-bubbles from the space above and around $g'g'$. Numerous small holes drilled through the upper and outer edge of $g'g'$ were intended to make, and probably did make, this operation more effective,

Most of the water (80 to 85%) coming up through t' passed down and out by way of the double funnel $f'f'$, but in order to remove the air-bubbles a certain amount of overflow was maintained through seven small tubes leading obliquely upward and outward from the water space at the edge of $g'g'$. One of these overflow tubes is shown in the figure at the left. Each of them was connected with a small rubber tube, and the outer end of each rubber tube was about 2 cm. higher than the top of hh. Whenever the tube t' and the block $g'g'$ were being agitated to remove air-bubbles, as before described, the main outlet o' was closed, so that all the water which passed under the disk had to escape by the overflow tubes. This method of getting rid of air-bubbles was adopted after the problem had been studied by means of a kind of dummy apparatus, in which the disk S was replaced by a plate of glass. There is reason to believe that it was fairly effective, but it was cumbrous, and probably a different arrangement will be used in future work. No similar device appeared to be necessary for the space immediately above the disk, as air-bubbles originally there would naturally be carried upward through the tube t by the escaping water. A single overflow tube, q, led out from the double funnel $f\,f$, by which the water was brought to the upper surface of the disk, and through this tube a small overflow was maintained to carry off bubbles that might otherwise have caused trouble. Another function of q was to serve as a kind of gauge

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indicating roughly the amount of pressure exerted by the water within the apparatus, some parts of which were not well calculated to bear a great disruptive force.

The copper wire w, about 0.016 cm. in diameter, leads from a point on the upper copper coating of the disk through a hole in h, where it is held in a water-tight joint between a hard rubber peg and a soft rubber sheath surrounding the peg, to a wooden shelf, where its end is gripped between two copper washers under the head of a screw, all of which objects are shown in the figure. A thicker copper wire, about 0.06 cm., one end of which is pinched between the upper washer and the head of the screw, leads off toward a galvanometer. Another thin copper wire, w', similar to w, starting from a corresponding point on the under copper coating of the disk, passes through h' and is fastened at its outer end exactly as the wire w is fastened. It is necessary to consider these details, for one can easily imagine a method of connecting the fine wires with the thick wires that would give rise to very disturbing thermo-electric forces and make the whole investigation useless.

At first the copper wires w and w' were *soldered* to the copper faces of the disk, as little solder as possible being used, with the hope that the thermo-electric forces at the top and bottom of the very thin layer of solder used would be very small in comparison with the large thermo-electric forces due to the copper-steel junctions. But this hope was not justified. The disturbance arising from these soldered junctions was very serious. The fact appears to be that each copper wire, exposing on the whole a surface of many square millimeters to the water, kept its point of attachment with the *solder* much warmer or much colder, as the case might be, than the same point would have been kept by direct contact with the water. The effect is similar to that observed when a soldered junction between two copper wires, one thick and one thin, is held a short distance beneath the surface of water differing considerably in temperature from the air above it. In such a case, represented by Figure 2, the submerged part of the thin wire, and also its point of attachment with the layer of solder, has very nearly the same temperature as the water; but the submerged part of the thick wire does not so nearly attain this temperature. The result is a difference of temperature between the two points of attachment with the solder, and a consequent thermo-electric effect, which an unwary observer might attribute to difference in the thermo-electric quality of the two wires. If

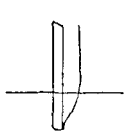

FIG. 2.

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in such a case the junction is pushed deep beneath the surface, the observed effect is diminished and perhaps disappears.

Accordingly it was necessary to get rid of the soldered junctions upon the disk. Therefore the device was adopted of attaching the copper wires to the copper surfaces by means of copper electrolytically deposited. The details of the operation, where one junction only is to be dealt with, are as follows: Cover the surface of the disk, in the neighborhood of the spot where the junction is to be, with a thin layer of some non-conducting substance, paraffine for instance, and then scrape off this coating from a patch about 0.5 cm. long and 0.1 cm. wide. Coat also, with a non-conducting substance, the copper wire, and then scrape one end of it bare for a distance of about 1.0 cm. Lay the bare part of the wire along the middle of the bare strip on the copper disk and press it down flat in that position, the end of the wire projecting a little beyond the limits of the bare strip. While holding the wire firmly in place, attach it near each end of the bare strip by melting at each spot a bit of paraffine. A few drops of sulphate of copper* are now placed upon the bare part of wire and disk, above which they stand in a little mound, as in Figure 3. Another copper wire, the lower end of which dips a little distance into the mound of liquid, serves as the anode in the electrolysis. The exposed surfaces at the bottom of the liquid are the cathode, the current being carried off, not through the thin wire, but through the body of the disk, to another wire not here shown, the intensity of current aimed at being 0.02 ampere per sq. cm. of the exposed surface of the cathode. A run of three or four hours makes the junction sufficiently strong for proper use, though perhaps it is safer to let the action go on longer. After the deposit is completed the protruding end of the fine copper wire is cut off and the paraffine surrounding the junction is scraped away. When several junctions upon one side of the disk are to be formed, it is easy to make the deposit upon all of them simultaneously.

In the final use of the apparatus the copper wires must be kept from contact with the copper surface of the disk at other points than the legitimate junctions. Accordingly the wires and the disk were coated with a thin layer of asphaltum varnish, baked on at a temperature above that to which the apparatus was to be exposed in the conduction experiments.

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* Of specific gravity 1.10, with 20 drops of strong H_2SO_4 added to 200 cu. cm. of the solution.

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There are thirteen of these fine wire junctions on each side of the disk, those on the upper side being arranged and numbered as shown by Figure 4. On the under side are corresponding junctions, 1′ just beneath 1, 2′ just beneath 2, 3′ just beneath 3, etc. The method of combining these junctions and the method of estimating the mean difference of temperature between the two copper-steel surfaces, by means of the thermo-electric currents sent through these junctions to a galvanometer, will be described later.

The parts j_1 and j_2, in Figure 1, are copper-German-silver junctions. The German-silver wire $g\ s$, about 0.015 cm. in diameter, is continuous from one junction to the other. At each junction the German-silver wire is joined to a copper wire, about 0.010 cm. in diameter. From each junction the two wires, separated by a strip of plastic non-conducting material ("Jenkin's packing"), y, are led into and along a plug, p, consisting of two half-cylinders of hard rubber held firmly together by clamps k and k. Within this plug the fine copper wire is attached in a soldered joint to another copper wire, W, about 0.06 cm. in diameter, which leads away toward a galvanometer. The loop of wire exposed to the water near each junction is coated with varnish to prevent disturbance due to chemical action. Shellac, baked on, seems best for this purpose. The water, as the arrows indicate, passes j_1 on entering, and j_2 on leaving, the upper chamber of the apparatus. The thermo-electric current from these junctions shows, when interpreted, the difference of temperature of the incoming and outgoing streams.

The amount of water flowing through the apparatus per second, about 24 grams, was measured by noting the time required to fill a flask of known capacity, F, in Figure 5. This time was about 75 seconds, and it was observed at stated intervals by means of an ordinary watch. The devices used for making this flow nearly constant, for an hour or more at a time, will be described later.

JJ, in Figure 1, is a double-walled copper jacket, supported by means of lugs, l, l, upon the ring $b\ b$, a thick piece of rubber under the end of each lug preventing metallic contact with b. The water, after passing the junction j_2 on its way out, entered this jacket near the bottom, flowed around and upward and escaped by the orifice O into a descending tube, the lower end of which was kept at any desired level, usually lower than any point shown in the figure. Thermometer T_1, passed by the stream on its way to j_1, and T_2, in the jacket near the exit, gave a rough indication of the change of temperature suffered by the water between these two points. It was usually about 1° C. when

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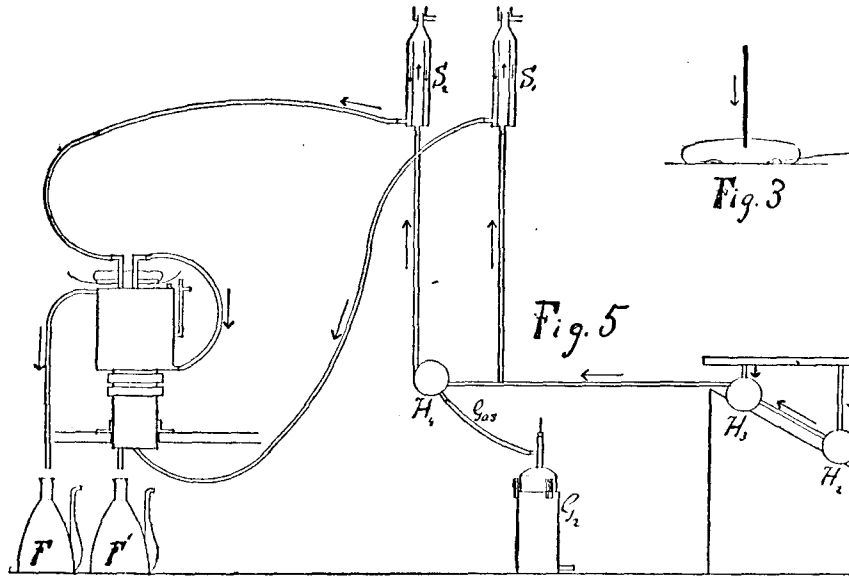

Fig. 5

Fig. 3

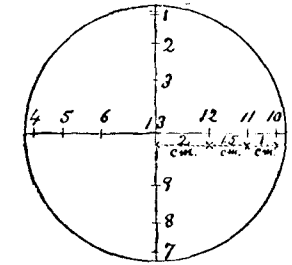

Fig. 4

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it was a fall, and somewhat less when it was a rise, as one would expect from the fact that the jacket was usually warmer than the air surrounding it. The mean temperature of the jacket probably differed in most cases less than 1° C. from the temperature of the double funnel, $f f$, which it almost completely surrounded. The space around $h\,h$ and $h'\,h'$ beneath the jacket, and the lower part of the jacket itself, was protected by a thick layer of cotton wool. The flat top of the jacket and the plugs and wires above it were protected in the same way. Under these conditions, the cooling or heating of the water by radiation or absorption at its envelopes between j_1 and j_2 was probably exceedingly small. As a further precaution against error from this source (and from certain other possible currents due to chemical action at j_1 and j_2, for instance), the stream passing through the upper chambers of the apparatus and over the upper surface of the disk was alternately made warmer and colder than the stream passing across the under surface of the disk.

The water-jacket $J J$ was open to the air at A to allow the escape of air-bubbles, which would otherwise have accumulated to such an extent as to affect the flow of water at O. Another outlet, at E, served as an overflow when the water came too fast to be delivered wholly through O. The streams from O and E were joined in the flask F, Figure 5. These minutiæ are of much importance, as the need of great uniformity in the rate of flow is imperative.

The general arrangement of the apparatus, with the exception of the electrical appliances, is shown in Figure 5. H_1, H_2, H_3, and H_4 are very effective contrivances * for heating a stream of water by the combustion of gas, which is supplied at constant pressure through two gasometers G_1 and G_2, one of which is shown in section. The water, which came from a large tank at the top of the Laboratory, with great regularity of flow when uninterrupted by obstructions in the apparatus, and at a nearly constant temperature, passed through the three heaters, H_1, H_2, and H_3 without division. Between H_3 and H_4 the stream divided, one part, about one half, going through H_4 to the standpipe S_2, the other part going without further heating to the standpipe S_1. These standpipes, from which a continual small overflow was maintained, had the double function of maintaining a constant head for the flow of the two streams through the conduction apparatus, and sifting out much of the air, which the heating had driven out of solution

* Made by the Buffalo Dental Manufacturing Company, No. 347 of their Catalogue for 1895.

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in the water. With the arrangement shown in Figure 5 the warmer stream of water enters the upper chamber of the conduction apparatus, and the cooler stream enters the lower chamber. This arrangement was, however, used alternately with another, in which the water entered S_1 after leaving H_4, the warmer stream going in this case to the lower chamber of the conduction apparatus. One stream was usually about 10° C. warmer than the other.

It is now time to describe and discuss more fully the electrical devices and apparatus used for measuring, 1st, the difference in temperature of the two sides of the steel disk, and, 2d, the difference in temperature of the incoming and outgoing water of the upper chamber of the conduction apparatus.

Calibration of the Copper-Steel Thermo-electric Elements.

It has been stated that there were thirteen copper wires leading off from each copper coating of the steel disk. Each pair of wires, one above and the corresponding one below, represents a copper-steel thermo-electric element, consisting of a piece of steel about 0.3 cm. thick between two pieces of copper. To calibrate these elements *in situ*, that is, to determine by direct trial upon the disk the e. m. f. corresponding to a given difference of temperature between the upper and lower surfaces of the iron, is apparently impossible. Accordingly, two slender bars, one about 1 square millimeter in cross section, the other about one third as large in cross section, and each 7 or 8 cm. long, were cut from the same plate of steel from which the disk had been made, and tests were made with these,* copper wires having been soldered to the ends. The apparatus used for these tests is shown in Figure 6. B_1 and B_2 in this figure are vertical brass tubes through which streams of water at any desired temperature may be made to run. T_1 and T_2 are Baudin thermometers, remarkably similar in size

* Experiments, in which a thin bar of steel, of the same quality as those here described, was subjected to longitudinal and to torsional stress, showed its thermo-electric quality to be very little affected by such conditions. Fearing, however, lest the *disk*, which had been subjected to certain processes which the thin bars had not suffered, might differ from them in thermo-electric quality, I have recently cut from the rim of a duplicate disk, made at the same time as the other, two narrow strips, which I have compared directly with the thinner of the two bars used in the copper-steel tests. These strips proved to be so like the bar in thermo-electric quality that it was difficult to make out with certainty any difference between them.

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and reading nearly alike at all temperatures, each graduated to 0°.2 C. The steel bars b and b', and the copper wires soldered to them, extend through the rubber stoppers r_1 and r_2, so that the ends are exposed to the streams of water for a distance of about 1.3 cm. To prevent disturbance from chemical action upon the steel and copper, the parts exposed to the water had been dipped in a solution of copal in ether. With this protection of the junctions it appeared from tests made at various temperatures that there was no chemical action of sufficient magnitude to affect materially the results of the experiments made to determine their thermo-electric behavior. The tests for chemical action were made by exposing both ends of one bar to water at the same temperature, sometimes with the bar *in situ*, as in Figure 6, and sometimes not.

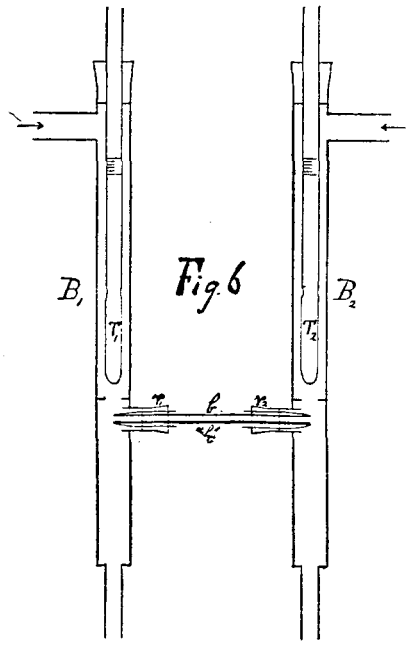

Fig. 6

The difference of temperature used in the thermo-electric tests was commonly about 4° C. The thermometers were read, by means of a telescope, to one tenth of one division, that is, to 0°.02. To eliminate disagreements of the thermometers, and various other possible sources of error, the streams were regularly interchanged, other conditions remaining the same. Thus, if a set of observations had been made with T_1 reading 28° and T_2 reading 24°, another would immediately be made with T_1 reading about 24° and T_2 about 28°.

The following course of reasoning will show how this method of using the thermometers tended to eliminate their errors from the result. Let us suppose that T_1 is used at 24° and T_2 at 28°, then T_1 at 28° and T_2 at 24°, and that afterward T_1 is used at 66° and T_2 at 70°, then T_1 at 70° and T_2 at 66°. Let $[E_1]_{20}$ be the error of T_1 at 20°, etc. Then we have in the various cases supposed: —

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	True Difference of Temperature.	Error.
1st case	$28 + [E_2]_{28} - 24 + [E_1]_{24}$	$[E_2]_{28} - [E_1]_{24}$
2d case	$28 + [E_1]_{28} - 24 + [E_2]_{24}$	$[E_1]_{28} - [E_2]_{24}$

$$\text{Error of mean} = \tfrac{1}{2}\,([E_1]_{28} - [E_1]_{24}) + \tfrac{1}{2}\,([E_2]_{28} - [E_2]_{24})$$

Similarly, the error of the mean at the higher temperatures is

$$\tfrac{1}{2}\,([E_1]_{70} - [E_1]_{66}) + \tfrac{1}{2}\,([E_2]_{70} - [E_2]_{66}).$$

If the "error of the mean" had been equally great at all observation stages on the thermometers, it would have affected the absolute value of the result obtained for the sensitiveness of the copper-steel thermo-electric element, but would have left unaffected the ratio of the sensitiveness at one temperature to that of any other temperature. Calibration of the thermometers showed that the "error of the mean" was not the same everywhere on the thermometers. The variation, though small, was perceptible, and might, if neglected, make the interval called 4° at one stage one half of one per cent greater or less than the interval called 4° at another stage. This error would not be very serious in view of the general character of the experiments if it had its full effect; but, in fact, the conclusion as to the conductivity of the steel depended upon the ratio of the sensitiveness of the copper-steel element at any temperature to that of the copper-German-silver element at or near the same temperature. Both kinds of element were calibrated by means of the same thermometers, and therefore the chance that final error of any magnitude could result from neglect of the errors of the thermometers is exceedingly small. Accordingly, such errors were neglected, the thermometers being used as if correct.

The question of course arises whether the two junctions differed in temperature just as much as the two thermometers did. It is no doubt true, that, when temperatures much above those of the room were used, each of the steel bars, several centimeters of which were exposed to the air, was a little cooler at each end than the water flowing past it. This difference was probably small, and must have been about the same at each end. The disturbance, or inaccuracy, caused by it should be smaller with the slender bar than with the other. Accordingly the slender bar was used most of the time, and all the results but one recorded in the following table were obtained with it. On the last day of the observations on copper-steel junctions one of the junctions on this bar broke. Then the thick bar was substituted for

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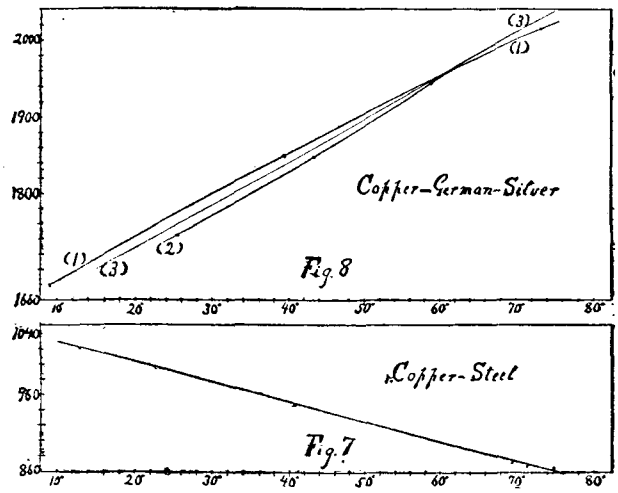
the other, and the result given for the temperature 74°.9 was thus obtained. This result agrees well enough with the others to indicate that there was no large difference in behavior of the two bars at the high temperatures. Previous trial had shown that they gave nearly equal effects at low temperatures. The one value here given for the thick bar was used with the others, obtained with the thin bar, in plotting the calibration line, Figure 7, for copper-steel junctions.



The electric currents were measured by means of a fairly sensitive astatic galvanometer, the reduction factor of which was frequently determined by use of a current of known strength.

Copper-Steel Junctions.

Date.	Temperature of Room.	Mean Temperature of Junctions.	E. M. F. per 1° C. Diff. of Temp. of Junctions.
	°	°	
Sept. 25, 1894	21	22.6	994×10^{-8} volts.
Nov. 9, "	12	12.7	1019 "
" 16, "	14	11.8	1019 "
Dec. 8, "	13	11.2	1034 "
Nov. 9, "	13	36.1	965 "
Dec. 8, "	13	40.6	949 "
Nov. 16, "	15	71.4	868 "
Dec. 8, "	13	69.5	873 "
" 12, (?) "	13.5	74.9	866 "

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With these data the line given in Figure 7 was obtained. It is a straight line, the inclination of which indicates a neutral point in the neighborhood of 400° C.

Calibration of Copper-German-Silver Junctions.

It has already been stated that junctions of copper and German-silver were used to measure the difference of temperature of the incoming and outgoing water of the upper chamber. These junctions, held firmly in the plugs *p*, *p*, of Figure 1, were tested in the same apparatus and by the same method that had been used with the copper-steel junctions, the ends of the plugs fitting into the short side tubes occupied by rubber stoppers in Figure 6. The results presently to be recorded were obtained with two pairs of junctions called respectively No. 1 and No. 2. The same piece of german-silver wire was used in both pairs. The copper wires of No. 2 were not the same as those of No. 1, but all were taken from the same spool, that is, all had once been parts of one continuous wire.

The following method was sometimes used in making the junctions. The German-silver wire was heated in melted paraffine to the neighborhood of 230° C., the object being to forestall any change of its properties which might otherwise take place in the heat of soldering. In order to make sure that this temperature was not exceeded in the soldering, a bath of melted paraffine of about the same temperature was used to heat the soldering "iron." This device was abandoned after a time, experience seeming to show that it was unnecessary, and the junctions of Nos. 1 and 2, just mentioned, were not made in this way. The junctions of No. 1 were not coated with copal to protect them against chemical action of the water, but rosin was used in making this pair of junctions, and this left a partial coating which gave considerable protection. Experiments had appeared to show that a protective coating was not necessary. A test for disturbance due to chemical action with this pair of junctions was satisfactory, no evidence of such an effect being found. In making No. 2, however, the junctions were carefully coated with shellac, dried on at a temperature of about 80°. All of the conduction experiments of which the results will be given in this paper were made with No. 2, except those of August 13, which were made with a similar pair.

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Copper-German-silver Junctions.

Junctions.	Date.	Mean Temperature of Junctions.		E. M. F. in Volts per 1° C. Diff. of Temp. of Junctions.		
No. 1	Dec. 27, 1894	9°.6		1668 × 10^{-8}		
"	" 28, "	9.6	9°.2	1677	"	1679 × 10^{-8}
"	Jan. 1, 1895	8.4		1691	"	
"	Dec. 28, 1894	39.7		1858	"	
"	Jan. 1, 1895	39.3	39°.5	1838	"	1848 "
"	Dec. 28, 1894	73.6		2007	"	
"	Jan. 1, 1895	73.2	73°.4	2022	"	2015 "
No. 2	Aug. 29, 1895	25.4		1746	"	
"	" "	43.4		1849	"	
"	" "	59.1		1936	"	

August 31, 1895, further observations were made on No. 2 at 25°.4 and at 59°.2, but they were comparative only, as the reduction factor of the galvanometer was not determined on this day. If we *assume* the effect at 25°.4 to have been the same as on August 29, we get

No. 2	August 31	25.4	1746
"	"	59.2	1951

It is found by interpolation that No. 1 would give for

25.4	1772
43.4	1871
59.1	1949

The differences between the results obtained with the two pairs of junctions are probably within the limits of experimental error, and it appears better to use the results from both pairs in plotting the calibration curve than to use those from No. 2 only. No great accuracy is claimed for the absolute values obtained in any of the calibration tests. The calibration curve of No. 1 is shown as No. 1 in Figure 8. It is very slightly convex upward. The observations of August 31, reduced to absolute measure by means of the assumption already stated, are used, with those of August 29, to give data for the calibration curve of No. 2. This curve, No. 2 of Figure 8, is very slightly

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concave upward. Line No. 3, a mean between No. 1 and No. 2, is practically a straight line, which, if continued, would indicate a neutral point in the neighborhood of the absolute zero. In subsequent work this straight line is assumed to be correct, and data needed for use in the conductivity calculations are taken from it.

The Electric Circuits.

Figure 1 shows that the fine copper wires connected with the upper and under copper coatings of the steel disk led out to connections with heavier copper wires on a wooden shelf surrounding the apparatus carrying the disk. Some slight thermo-electric effect could be produced by warming one of these connections, but as the wires from both faces of the disk were connected here in the same way, the connections being all equidistant from the disk, the thermo-electric forces

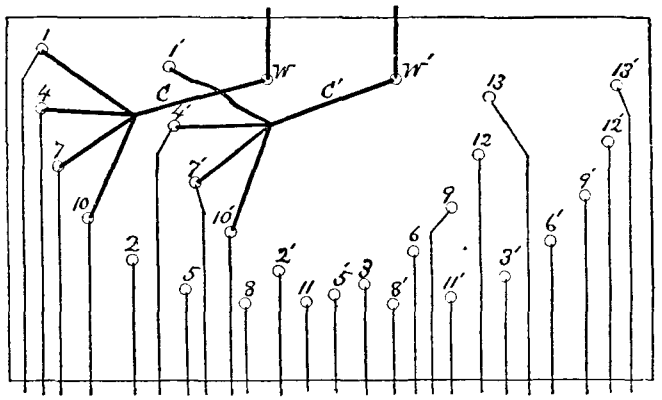

Fig. 9.

existing in them must have neutralized each other in the ordinary use of the apparatus. The copper wires leading away from these connections were all of the same length, size, and quality. They terminated in a kind of commutator, or switch-board, shown in Figure 9. The numerous small circles in this figure indicate small holes containing mercury. Holes 1, 2, 3, 4, etc. are connected, by means of the wires just mentioned, with junctions 1, 2, 3, 4, etc., respectively, on the disk. A connector, *C*, brings the four junctions 1, 4, 7, 10, which are (see Fig. 4) all at the same distance from the centre of the disk, into multiple arc, and takes the currents coming from them to one

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wire leading, through the mercury cup, W, to a galvanometer. Connector C' does the same for junctions 1′, 4′, 7′, and 10′. The same connectors can evidently be used to bring junctions 2, 5, 8, 11, and 2′, 5′, 8′, 11′ into action, or 3, 6, 9, 12, and 3′, 6′, 9′, 12′. The central junctions, 13 and 13′, were used by themselves.

The apparatus, beyond this switch-board, does not require detailed description. The resistance coils used were reduced to legal ohms by comparison with those of an Anthony standard (Queen & Co.). Thermometers at two or three points along the circuit gave such account of the temperature as was necessary. The galvanometer was a Thomson astatic, with a concave mirror. The strength of current required to produce a deflection of 1 cm. on the scale was about 12×10^{-8} amperes.

The circuit containing the copper-German-silver junctions, j_1 and j_2 of Figure 1, is simpler and requires little further description. The galvanometer of this circuit had a plane mirror, and was used with telescope and scale. Its sensitiveness to a given current was about the same as that of the first galvanometer. The circuit included, at a point corresponding to the switch-board of the other circuit, mercury cups at which the connection could be broken.

In addition to the mercury cups already mentioned, each circuit included a mercury commutator, by means of which the course of the current in the galvanometer could be reversed. These mercury cups and commutators were a source of much disturbance, and toward the last of the work solid metallic connections were in some cases substituted for them. The difficulty was thermo-electric. If two copper wires run into the same mercury cup at different levels, or if the two wires are of different size or different external condition, there will be at the copper-mercury junctions, unless the temperature of the room is more than usually uniform and constant, thermo-electric effects which cannot be neglected in delicate measurements of electric current. There was a certain approach to uniformity in these disturbances, which made it possible to eliminate them in great part from the result by the device, already described, of running the warmer stream of water alternately above and beneath the disk. The full measure of this source of error was, however, not realized until the last week or two of the work, and it may be that the discordance between the results of August 13 and 15 and those obtained later was due to lack of care in protecting the copper-mercury junctions from changes of temperature on the days mentioned.

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Greater vigilance, and probably greater accuracy, marked the later work.

The difficulty here discussed can be very much reduced by a more sparing use of gas flames in the room.

The Observations.

As an example of the observations in the main experiment, showing their character and their arrangement, the last set made will now be given, some unimportant details being omitted.

The letters L and R refer merely to the position of the commutators. A change from L to R reverses the current in the galvanometer concerned. In each circuit the first observation is made under L, the second under R, the third under L, etc.

The note "1, 4, 7, 10," means that the junctions of the outer circle of the disk (see Fig. 4), both above and below, are in use, connected as in Figure 9. After this set of junctions, those of the next circle, 2, 5, 8, 11, are used, etc.

Each group of seven or five observations in the first circuit was made between two groups of three observations in the second circuit. Before the first, third, fifth, etc., groups of *three* in the second circuit, the main outlet of the water from the lower chamber of the apparatus was closed for a few seconds to wash out, through the overflow tubes (Fig. 1), the air-bubbles that might have accumulated beneath the disk. This operation did not greatly affect the current in the second circuit. The course of operations gave the first circuit about two minutes for recovery after the disturbance before observations in this circuit were renewed.

The water had been running through the apparatus for about an hour, as usual, before the observations began.

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Junctions.	Copper-Steel Circuit. L.	R.		Copper-German-silver. L.	R.	
1, 4, 7, 10	36.28	30.76		46.98	40.85	6.09
	36.20	30.80	5.40	46.90		
	36.14	30.80		46.82	40.92	5.94
	36.15			46.90		
2, 5, 8, 11	35.80	31.04		46.94	40.85	6.07
	35.78	31.04	4.73	46.90		
	35.76	31.06		46.95	40.86	6.05
	35.78			46.87		
3, 6, 9, 12	35.15	31.58		46.84	40.78	6.07
	35.14	31.58	3.54	46.86		
	35.10	31.61		46.90	40.88	6.05
	35.11			46.96		
13	34.78	31.95		47.02	40.95	6.06
	34.80	31.91	2.88	47.00		
	34.84			46.85	41.00	5.88
				46.91		
3, 6, 9, 12	35.12	31.60		46.70	40.98	5.81
	35.10	31.58	3.54	46.88		
	35.14	31.56		46.75	41.10	5.68
	35.10			46.81		
2, 5, 8, 11	35.70	30.92		46.78	41.10	5.66
	35.68	30.98	4.73	46.74		
	35.66	30.96		46.80	41.14	5.61
	35.66			46.70		
1, 4, 7, 10	35.98	30.70		46.76	41.30	5.43
	35.90	30.66	5.25	46.70		
	35.90	30.70		46.65	41.18	5.47
	35.98			46.65		
					Mean,	5.85

Time occupied, 5:39 to 6:35 = 56 minutes.

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The following observations accompanied those just recorded: —

t = temperature of water running from lower chamber.
t_1 = " " at thermometer T_1, Fig. 1.
t_2 = " " " T_2, "
S' = number of seconds required to fill flask F', Fig. 5.
S = " " " " F, "

The capacity of each flask was about 1800 grams. The numbers in brackets in the column headed S' indicate the number of grams of water escaping per minute through the overflow tubes of the lower chamber. In the column S is a similar note for the upper chamber.

Time.	t	t_1	t_2	S'	S	
5:33	22°.0	32°.8	31°.9			
5:35				70.5	72.5	72.8
				[300]	73.0	
6:02	22°.0	32°.5	31°.7		72.5	
6:37	21°.8	32°.2	31°.4			
6:40				71	73.5	73.5
				[290]	73.5	
					[50]	
Means	21°.9	32°.5	31°.7	70.8	72.9	

The 50 grams per minute noted as the overflow from the upper chamber is disregarded, not because it is inconsiderable in comparison with the main stream, which carried about 1400 grams per minute, but because it was taken off without having been brought near the disk, so that its temperature must have been practically unaffected by its admission to the chamber.

Assuming, for our present purpose, that no corrections need be applied to the thermometer readings, we see that the water escaping from the jacket is about 0°.8 colder than it was when it entered the upper chamber, that the difference of temperature of the streams in the two chambers is about 10°, and that the temperature of the disk must be about half way between those of the streams, 27°, let us say. The main object in noting the difference between t_1 and t_2 is to get information as to the effectiveness of the jacket that surrounds the upper chamber. If, as in this case, the temperature of the jacket differs only 1°, or thereabout, from the temperature of the chamber, the protection afforded must be nearly perfect. Apparently the difference was little, if any, more than 1° in any case.

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The Calculations.

If the deflections obtained from the junctions at different points on the disk were all equal, or nearly so, the calculation of thermal conductivity from the observations would be exceedingly simple. Unequal as these deflections are, it would still be allowable to take their mean as representing the mean difference of temperature between the upper and lower surfaces of the steel disk, if all junctions represented equal areas of the disk; but this is not the case. The process of finding what the mean deflection would be, if all parts of the disk were equally represented, is indicated by the following formula, in which Δ stands for the mean deflection desired; δ for the deflection given by a particular pair of junctions; σ for the area of cross-section represented by this pair of junctions; S for the area of one face of the disk: —

$$\Delta = \frac{\Sigma\, \delta\, \sigma}{\Sigma\, \sigma} = \frac{\Sigma\, \delta\, \sigma}{S}.$$

If there were many pairs of junctions, but only one pair at a given distance, r, from the axis of the disk, each pair would represent a certain ring-shaped portion of the disk, the area of which at either surface is $2\,\pi\, r \times dr$. Writing this expression in place of σ, and calling the radius of the disk R, we get

$$\Delta = \frac{\Sigma\, \delta\, \sigma}{S} = \int_0^R \frac{\delta \times 2\,\pi\, r \times dr}{S} = \frac{2\,\pi}{S} \int_0^R \delta \times r \times dr.$$

We can approximate to this integration by means of a graphical process, making use of the data given by the observations actually made. From the series of observations given on page 290, we get the following values: —

r	δ
0	2.88
2 cm.	3.54
3.5 "	4.73
4.5 "	5.33 $[= \frac{1}{2}\,(5.40 + 5.25)]$

The observed value of δ for $r = 0$ is to be increased a little to make allowance for the fact that the resistance of the circuit, including junctions 13 and 13′, was somewhat greater than the resistance of the

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circuit when the other junctions were in use. Making this slight change, and then taking the values of r as abscissas, and the values of δ as ordinates, we get the four determining points of curve A in Figure 10. Taking various ordinates from this curve, and multiplying each by the corresponding value of r, and, for convenience in plotting, by 0.2, we get the determining points of the curve a. The area under this curve is evidently

$$0.2 \int_0^R \delta \times r \times dr,$$

from which the value of Δ is at once obtained. In this case $\Delta = 4.52$. The mean of the observed values of δ in the series under discussion is 4.12. All this is for the case where the water above the disk was warmer than that below the disk, on September 2.

The same day another series of observations was made, with the warmer stream beneath the disk. The curves B and b (Fig. 10) have to do with this second series of observations. They give for the value of Δ, 4.60.

It is assumed in the subsequent calculations that Δ is equal to the deflection which would be obtained from any pair of junctions on the disk, one above and one below, if the difference of temperature were made, for all values of r, equal to the difference between the mean temperature of the whole upper face and the mean temperature of the whole lower face of the steel disk. The validity of this assumption will be discussed later.

In the calculation presently to be made, the subscript 1 will have reference to the circuit containing the junctions on the disk; the subscript 2 will have reference to the circuit containing the copper-German-silver junctions.

The test for "sensitiveness" of the galvanometers, which has not been described at length, was made by running the same current through the two simultaneously. The "reduction factor," by which the deflection in centimeters must be multiplied to give the strength of this current in amperes, might be given for each galvanometer in numerical terms; but it will be evident that, for the calculation in hand, it is necessary to know only the ratio of the two reduction factors, which is the reciprocal of the observed simultaneous deflections of the two galvanometers in the sensitiveness test.

In finding the value of m, allowance is made for the change of capacity of the measuring flask with change of temperature of flask and water.

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We have: —

k = the thermal conductivity in c. G. s. units.

Q = number of heat units flowing through disk in one second;

T = thickness, in centimeters, of the steel disk;

S = area, in square centimeters, of horizontal cross-section of the steel disk;

t = mean difference in temperature of sides of steel disk;

m = mass, in grams, of water traversing upper chamber per second;

Δ_1 = mean deflection in circuit 1, as before described;

Δ_2 = mean deflection in circuit 2, in conduction test;

R_1 = reduction factor of galvanometer 1;

R_2 = reduction factor of galvanometer 2;

d_1 = mean deflection of galvanometer 1 in sensitiveness test;

d_2 = mean deflection of galvanometer 2 in sensitiveness test;

$[R_1 \times d_1 = R_2 \times d_2$, and so $R_1 \div R_2 = d_2 \div d_1]$;

E_1 = e. m. f., in volts, of copper-steel element per 1° C. difference of temperature;

E_2 = e. m. f., in volts, of copper-German-silver element per 1° C. difference of temperature;

r_1 = resistance, in legal ohms, of circuit 1 in conduction test;

r_2 = resistance, in legal ohms, of circuit 2 in conduction test;

Then

$$k = \frac{Q \times T}{S \times t} = \frac{m \times \frac{\Delta_2 \times R_2 \times r_2}{E_2}}{S \times \frac{\Delta_1 \times R_1 \times r_1}{E_1}} \times T$$

$$= \left(m \times \frac{\Delta_2}{\Delta_1} \times \frac{R_2}{R_1} \times \frac{r_2}{r_1} \times \frac{E_1}{E_2} \right) \times \frac{T}{S}$$

$$= \left(m \times \frac{\Delta_2}{\Delta_1} \times \frac{d_1}{d_2} \times \frac{r_2}{r_1} \times \frac{E_1}{E_2} \right) \times \frac{T}{S}.$$

Using this formula with the data for series A and B of September 2, we have: —

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A (warm water above.)			*B* (warm water below.)		
		log.			log.
$m = 24.57$		1.3904	$m = 24.58$		1.3906
$\Delta_2 = 5.85$		0.7672	$\Delta_2 = 4.91$		0.6911
$d_1 = 10.48$		1.0204	$d_1 = 10.48$		1.0204
$r_2 = 28.15$		1.4495	$r_2 = 28.14$		1.4493
$E_1 = 985 \times 10^{-8}$ [26°.9]		$\bar{6}.9934$	$E_1 = 985 \times 10^{-8}$ [27°.1]		$\bar{6}.9934$
	log.	$\bar{1}.6209$		log.	$\bar{1}.5448$
$\Delta_1 = 4.52$	0.6554		$\Delta_1 = 4.60$	0.6625	
$d_2 = 8.38$	0.9191		$d_2 = 8.30$	0.9191	
$r_1 = 16.58$	1.2196		$r_1 = 16.58$	1.2196	
$E_2 = 1796 \times 10^{-8}$ [32°.1]	$\bar{5}.2543$	$\bar{2}.0484$	$E_2 = 17.39 \times 10^{-8}$ [21°.8]	$\bar{5}.2403$	$\bar{2}.0415$
		1.5725			1.5033
$\frac{T}{S} = \frac{0.2952}{77.9}$		$\bar{3}.5786$			$\bar{3}.5786$
		$\bar{1}.1511$			$\bar{1}.0819$

$\bar{1}.1511$ = log. of 0.1416 = log. of k_a
$\bar{1}.0819$ = log. of 0.1208 = log. of k_b
Mean = 0.1312 = k

Thus, according to the observations of September 2, the conductivity of the steel at 27° C. is 0.1312.

The difference between k_a and k_b is large in this case, but it has already been explained that neither is intended to be complete by itself. The mean of the two is necessary to eliminate certain errors which have been discussed. It may well be doubted whether this elimination is perfect when the difference between k_a and k_b is so large. It will presently appear that the difference was exceptionally large on September 2.

The following table includes *all* the results obtained with the apparatus in its final condition. It has already been stated that the results of August 13 and August 15 do not agree with those found later, and a possible reason for this has been given, namely, lack of sufficient precaution, in the earlier experiments, against error from disturbing thermo-electric effects external to the conduction apparatus proper. Although the results obtained August 13 and 15 are here given, they are not included in finding the mean values given at the foot of each column. At one time it was suspected that an accumulation of dirt forming near the edge of the upper face of the disk, and checking the flow of heat there, might account for the discrepancy between the earlier and the later results. Accordingly, between August 28 and September 2 the conduction apparatus was dismounted, and the disk was cleaned and replaced. But the result obtained September 2 was in close agreement with most of the others.

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CONDUCTIVITY, k, OF OPEN-HEARTH STEEL IN C. G. S. UNITS.

Date.	Temperature.	k_a (Warm above.)	k_b (Warm below.)	k $\left(\frac{k_a + k_b}{2}\right)$	
Aug. 13, 1895	[27°.0]	[0.1463]	[0.1445]	[0.1454]	
" 17, "	27°.4	0.1301	0.1392	0.1347	
" 20, "	27°.8	0.1333	0.1334	0.1334	0.1347
" 22, "	26°.3	0.1334	0.1310	0.1322	
" 28, "	27°.4	0.1306	0.1310	0.1308	
Sept. 2, "	27°.0	0.1416	0.1208	0.1312	
Mean,	27°.2	0.1338	0.1311	0.1325	
Aug. 24, 1895	44°.2	0.1299	0.1343	0.1321	
Aug. 15, "	[62°.8]	[0.1264]	[0.1463]	[0.1364]	
" 17, "	59°.8	0.1242	0.1347	0.1295	
" 22, "	59°.0	0.1301	0.1287	0.1294	0.1316
" 26, "	58°.8	0.1296	0.1327	0.1312	
Mean,	59°.2	0.1280	0.1320	0.1300	

DISCUSSION AND CRITICISM.

Taking 0.1325 * as the value of k at 27°.2, and 0.1300 as the value at 59°.2, we get as the coefficient of change with rise of temperature

---

* Winkelmann's *Handbuch der Physik*, 1895, gives: —

Metal.	Temp.	k	Observer.
Eisen	0°	0.1655	Lorenz.
"	0°	0.1988	Angström.
"	über 0°	0.1587	Berget.
"	ca. 15°	0.1648	Neumann.
"	ca. 15°	0.1133	Wiedemann u. Franz.
"	0°	0.1509	Mitchell.
"	0°	0.172	Stewart.
Schmiedeeisen	0°	0.2070	Forbes.
"	39°	0.1485	H. F. Weber.
Stahl hart	ca. 15°	0.062	F. Kohlrausch.
" weich	15°	0.111	"
" "	15°	0.1104	Wiedemann u. Franz.
Puddelstahl	15°	0.1375 – 0.1418	Kirchoff u. Hausemann.
Bessemer stahl	15°	0.0946	" "
Mangan stahl	0°	0.03280	Mitchell.

It is probable that open-hearth steel resembles the iron of this table more nearly than it does the steel.

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$$\gamma = \frac{0.1300 - 0.1325}{0.1325 \times (59.2 - 27.2)} = -0.0006-.$$

If we take the values 0.1347 and 0.1316, obtained by including the bracketed values in finding the means, we get $\gamma = -0.0007+$. The value -0.0006 is to be preferred, although it is evident from the preceding pages that no great confidence can be placed in the digit of this coefficient. A wider range of temperature, a greater number of measurements, and evidently a more careful calibration of the copper-German-silver junctions is needed for a completely satisfactory determination of γ. Moreover, no allowance has here been made for the change in the specific heat of water between 27° and 59° C. It is to be observed that the lower temperature is very near the temperature of minimum specific heat of water. If it should be found that the specific heat of water at 59° is two per cent greater than at 27°, which is, to be sure, improbable, the value of γ obtained from these experiments would be 0. If the difference is one third of one per cent, which seems not unlikely, it will reduce γ to -0.0005. If we take this as the most probable value, it will, in spite of its uncertainty, be not devoid of interest, for the tables in Winkelmann give no values of γ in the case of steel, while for iron they give

$\gamma = -0.000038$ (Lorenz),
$\gamma = -0.000517$ (Angström),
$\gamma = -0.0011$ (Stewart).

The one measurement of k for an intermediate temperature, 44°.2, lies between the mean value for 27°.2 and the mean for 59°.2, which is gratifying evidence, so far as it goes, of the precision of the measurements.

It is a curious fact that every measurement of k near 27°, except the last, gave a smaller value than the preceding measurement. The reason for this is not evident.

At the low temperature the mean of k_a is a little greater than the mean of k_b. At the high temperature the contrary is true. In either case the difference is to be regarded as mainly accidental, and not significant, — a fact already mentioned and explained.

We must now consider more fully the question whether Δ, as deduced from curves like those of Figure 10, represents accurately the difference between the mean temperatures of the upper and of the under face of the steel disk. It can hardly be doubted that Δ, derived

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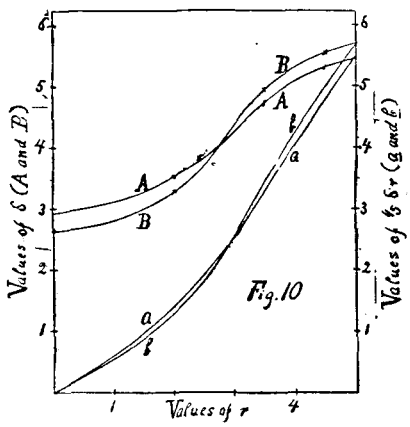
as it is from thirteen well distributed pairs of junctions, represents with considerable accuracy the mean difference of potential between the two faces of the steel disk; but is this mean difference of potential proportional to the mean difference of temperature between these two faces?



This question would be at once answered in the affirmative if the disk, instead of being metallically continuous, were made up of little columns of steel, in length equal to the thickness of the disk, tipped at both ends with copper, each column being insulated from its neighbors. For in such an aggregation there would be no short-circuiting, and the difference of potential at the two ends of any steel column would depend merely upon the difference of temperature at these ends; and, with the very small difference of temperature existing, only a fraction of one degree, the potential difference would be very strictly proportional to the temperature difference.

But the disk is continuous, and there must be short-circuiting currents within it. How will these currents affect the mean difference of potential of the two faces? These currents in the steel will be partly vertical and partly horizontal. We will consider, first, the vertical components. Let Figure 11 represent any two equal vertical elements, S_1 and S_2, of the disk, connected by the copper strips C_1 and C_2. Let the e. m. f. of element S_1 be E_1, directed upward, and the e. m. f. of S_2 be E_2, also directed upward, and let $E_1 > E_2$. If connection between elements were broken, the difference of potential betweeen the top and bottom of S_1 would be E_1, and that between top and bottom of S_2 would be E_2. The mean difference of potential would be $\frac{1}{2}(E_1 + E_2)$.

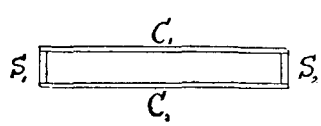


FIG. 11.

Let the resistance of S_1, equal to that of S_2, be called r. When connection exists, as in the figure, we have a short-circuiting current, C, passing up through S_1 and down through S_2. With this current, the difference of potential between top and bottom of S_1 is $E_1 - rC$,

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and the difference of potential between the top and bottom of S_2 is $E_2 + rC$. The mean of these two differences is $\frac{1}{2}(E_1 + E_2)$, the same value as if there were no short circuit.

If the element S_2, instead of being of the same size as S_1 had a cross-section n times as great, it would have n times as much weight as S_1 in reckoning the mean difference of potential, which would then be

$$\frac{1}{n+1}(E_1 + n\,E_2)$$

with open circuit, and

$$\frac{1}{n+1}\left[\left(E_1 - r\,C\right) + n\left(E_2 + \frac{r}{n}C\right)\right] = \frac{1}{n+1}\left(E_1 + n\,E_2\right)$$

with short circuit. This appears to show that the vertical components of short-circuiting currents within the steel disk do not affect the mean difference of potential between top and bottom.

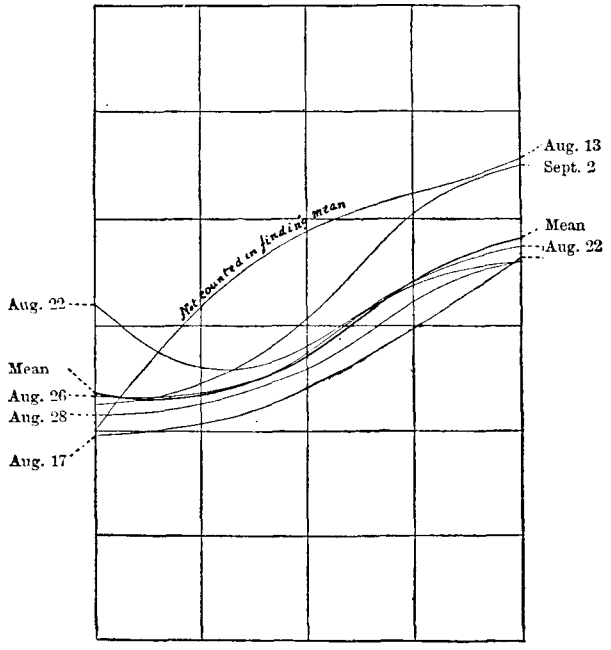

FIG. 12.

The non-effect of the horizontal components is shown by the consideration that a horizontal current, maintained in the disk by exter-

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nal or internal means, would have, of itself, no tendency to establish any mean difference of potential between the upper and under faces of the disk.

It appears, therefore, to be established that Δ does represent — that is, is proportional to — the mean difference of temperature between the upper and under faces of the disk.*

It may be of interest to compare the difference of potential curves of the various series of experiments. If in Figure 10 we take the mean of *A* and *B*, we get a new curve, which may be taken as representative of the potential conditions, or difference-of-potential condi-

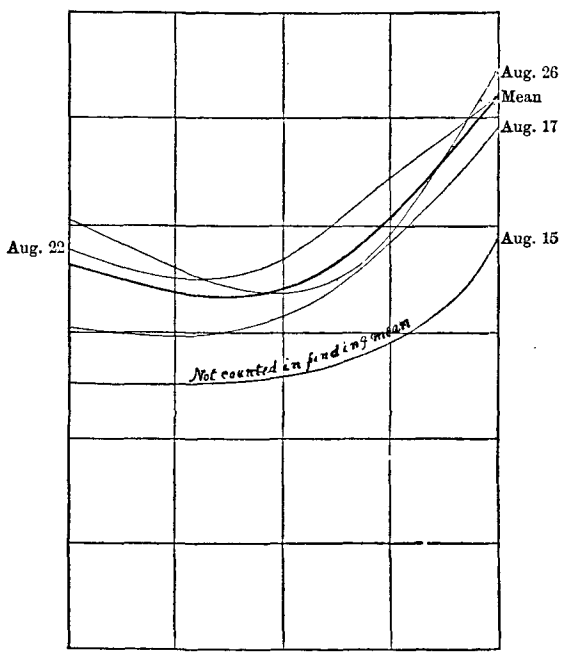

FIG. 13.

tions, prevailing in the experiments at low temperature on September 2. Combining each *A* curve for low temperatures with its corresponding *B* curve, and plotting the resultants, we get Figure 12, except the heavy line, which is obtained by taking the mean of all the others

* Cf. an article, by Prof. B. O. Peirce, "On the Properties of Batteries formed of Cells joined up in Multiple Arc." These Proceedings, Vol. XXX. p. 194.

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except that of August 13. This heavy line is, therefore, the typical difference-of-potential curve for low temperatures, about 27°. The heavy line of Figure 13 is similarly the typical curve for high temperatures, near 59°, the curve for August 15 not being used in obtaining this composite.

The difference between these two typical curves is noticeable. Each indicates that the greatest difference of potential is near the edge of the disk. Each shows a minimum about two thirds as great as the maximum, but the minimum of the high temperature curve occurs farther from the centre of the disk. The reason for this difference is not obvious. The rapidity of the flow of water was about the same for high temperatures as for low, but there was a greater tendency to development of bubbles in the warmer water, and this may have influenced to some extent the course of the water over the surfaces of the disk.

The low temperature curve of September 2 is in marked contrast with most of the others in its group, showing a relatively great difference of potential at the edge of the disk. It has already been stated that the copper coatings of the disk had been cleared of accumulated dirt shortly before the experiments of September 2. This dirt had lodged mostly near the edge of the disk, and its removal apparently had just the effect that would have been expected upon the flow of heat in that region. The value of k obtained September 2 accords well with those obtained shortly before the disk was cleaned.

As to the absolute values found for k, they are very likely in error to the extent of two or three per cent of their own magnitude, possibly more. A source of possible error not yet discussed is found at the ring which encloses the disk (see Fig. 1). The effective diameter of the disk is taken to be the distance through the ring and disk, from the groove on one side to the groove on the other. The ring itself in this grooved part is about 0.08 cm. thick. Its cross-section is about three per cent of the whole conductive cross-section. The material of the ring is very similar to that of the disk, if not quite the same. The uncertainty as to whether the thin part of the ring can properly be assumed to act like an equal portion of the disk itself, comes from the dubious nature of the approach to this part of the ring above and below. The flow into or from it may be partly lateral, through the edge of the disk proper, but it cannot be wholly so, for a narrow strip of the thicker portion of the ring is exposed to the water above and below the disk. It is not likely that the error here is large, but in future experiments a different method of supporting the disks will probably be used.

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It may be asked whether the method of investigation which has been described at such length in this paper will be applicable to the case of metals in general, and whether it can be extended through any large range of temperature. It is evident that the thermo-electric device for determining the difference of temperature between the two faces of the disk must be used with great caution, and will in some cases be difficult of operation; but its use is by no means restricted to iron. Copper and other metals thermo-electrically near it will certainly give some trouble, though it is believed that they can be successfully dealt with. It is probable that the range of temperature can be greatly increased by the use of other liquids instead of water; but if this is done, the question as to the specific heat of the liquid will become a difficult one.

The method described is a laborious one in its preparatory stages, but much of the initial work can be done by a mechanic. The operation of the apparatus, once prepared, is comparatively easy, and the calculations are simple. A single experimenter operates the whole machinery, and makes all the observations. He can make the A and B observations for a given temperature and calculate the value of k therefrom in one day, without excessive toil, and with a reasonable assurance that the result will be in accord with that of the day before.

This investigation was begun, at the author's suggestion, some years ago by Mr. A. W. Slocum, then a graduate student at Harvard, now of the University of Vermont. Mr. Slocum worked with great zeal and energy, and made substantial progress, but presently went abroad, leaving the research in my hands.

I have to thank all members of the Physical Department at Harvard, who have given me extremely valuable suggestions in regard to my work, and have furthered it by every means in their power.

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XVI.

THE OUTLINE OF CAPE COD.

By William Morris Davis.

Presented March 11, 1896.

Summary.

This essay attempts to restore the original outline of Cape Cod by reversing the processes at work on the present outline (p. 308). In order to gain good understanding of these processes, a review of previous accounts of the Cape is introduced (p. 304), a general consideration of the development of sea-shores is outlined (pp. 312–317), and the conclusions reached are applied to the problem in hand (p. 318). It is thus estimated that the land here once extended at most two or more miles into the sea on the east, and that perhaps three or four thousand years have been required for the retreat of the shore line to its present position (p. 326). This period cannot, however, be taken as a full measure of the time since the glacial deposits of the Cape were formed, for there is reason to believe that the land stood higher than now for an unknown interval between the building of the Cape and the assumption of the present attitude with respect to sea level.

The chief interest in the problem here discussed turns on the growth of the great sand spit of the "Provincelands" northwestward from the "mainland" of the Cape (p. 312), and on the protection thus afforded to the old cliffs of High head. Brief account is given of the growth and waste of the Provincelands (p. 323), and of the changes of the western shore line (p. 329). The essay closes with some practical suggestions regarding the protection of Provincetown harbor (p. 329), and some speculations concerning the future change of the Cape. The consumption of the north arm — from the elbow to the hand — will probably require about eight or ten thousand years (p. 331).

Introduction.

An excursion to Provincetown and the "mainland" of Truro on Cape Cod with the students of the Harvard summer course in Physical Geography, in July, 1895, brought to my attention a number of problems concerning the changes of outline suffered by the Cape. These problems had taken rough shape on the occasion of a visit to the peninsula several years ago. Supplementing the observations made on the ground by a study of the Coast Survey charts and by a review of what has been written on the subject, the following essay

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has gradually grown up. Its substance was presented before the Geological Society of America at the winter meeting in Philadelphia, December, 1895, and again before the Harvard Geological Conference in April, 1896.

The end of the Cape is pleasantly reached by a four-hour run in a steamboat from Boston across Massachusetts bay to Provincetown, in whose neighborhood the most significant of the features here described are to be found. By driving to High head, the northernmost point of the "mainland," a general view of the peninsula of Provinceland may be gained: thence driving or walking to Highland light, one may see a portion of the long harborless cliff that forms the "back" or eastern side of the Cape. Walking northwestward along the beach to Peaked hill life saving station, the action of the surf can be observed at leisure; and thence crossing the sandy belt to Provincetown, the varied forms of the dunes can be studied in detail. A second day may well include a visit to Race point, the northwestern extremity of the Cape, and a return southward along the wasting shore to Wood end, or Long point, whence the town can be regained by boat, previously arranged for.

Cape Cod is an excellent region for the study of shore forms in the light of their development from some antecedent outline, and their continued change towards some future state. Although the "mainland" of the Cape rises about two hundred feet above sea level, it is built of uncompacted clays and sands, with occasional boulders, and is therefore easily consumed by the waves. Standing far out beyond the general shore of New England, it receives a violent attack from storm waves, which alter the shore line so rapidly that the changes are measurable even in the short time covered by our records.

Extracts from Previous Writings.

The following extracts summarize a number of previous references to the Cape.

In the *Geology of Massachusetts* (I., 1841), E. Hitchcock makes brief mention of the erosion on the eastern coast and the growth of the Cape into Massachusetts bay (323), the southward growth of Nauset beach, a mile in fifty years (324), the dunes of Provincetown (325), and the "diluvial elevations and depressions" of Truro (367); Provinceland is "alluvial; that is, washed up by the ocean" (371).

Lieut. (afterwards Admiral) C. H. Davis wrote a "Memoir upon the geological action of the tidal and other currents of the ocean" (Mem. Amer. Acad., Boston, 1849, IV. 117–156), in which he called

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attention to the repeated occurrence along our coast of bars built northward from coastal bluffs, such as Sandy hook, N. J., and Cape Cod, and suggested that "a generic term" should be applied to these forms. He mentioned a place of division of the tidal currents on the east side of Cape Cod, near Nauset inlet, from which the flood tide flows north and south.

Thoreau's narrative of his excursions on the Cape in 1849, 1850, and 1855, tells of various changes in the coast line known to the people there. A log canoe, buried long before on the inner side of the bar that forms the eastern wall of the marshy East harbor at the north end of the mainland, was found many years afterwards on the Atlantic side of the bar; that is, the bar had been pushed westward over the buried canoe as the sea cut away the outer beach. Swamp peat was sometimes found on the exposed beach, although it was originally formed undoubtedly on the inside of the bar. Stumps had been seen off Billingsgate point; the implication being, not that the land had been depressed, but that it had been washed away, leaving the stumps mired in their native soil.* A writer in the "Massachusetts Magazine" of the previous century is quoted to the effect that an island, called Webbs island, formerly existed three leagues off Chatham, containing twenty acres of land; the people of Nantucket carried wood from it; but in the writer's day a large rock alone marked the spot, and the water thereabouts was six fathoms deep. (Cape Cod, in New Riverside edition of Thoreau's works, 1894, pp. 182, 183.)

Freeman's History of Cape Cod (1860) attributes much wasting of land to reckless cutting of the trees, — a doubtful conclusion as far as it refers to shore work, although probably applicable to the interior district of the dunes. He says: "The work of devastation was too extensively accomplished; as is seen on the shores of the Cape since washed away by tides aided by the force of the winds, so that vast flats of sand extend in some places a mile from the shore, now, at low water, dry, or nearly so, and in some instances these flats disclose large stumps of ancient trees embedded in their native peat" (752).

H. L. Whiting prepared a "Report on the special Study of Provincetown Harbor, Mass." (Rep. U. S. Coast Survey, 1867, pp. 149–157). He distinguishes Truroland, the mainland of the Cape, "by the

* I have found this explanation of the occurrence of tree stumps on the shoals off Chatham current among the fishermen of the Cape. See Proc. Bost. Soc. Nat. Hist., 1893, XXVI. 173.

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existence of clay and of boulders, and by the peculiar form of the 'bowl and dome' drift"; and Provinceland, "of sand only, — so free from all earthy matter that it will not even discolor water, — while the forms which the dunes and ridges here assume are mainly characteristic of wind drift" (155). He concludes that "the outer ridges of the peninsula of Provincetown were the earliest in date, and that the flats, marshes, and ponds now existing are subsequent accumulations and accidents, which have taken place under the shelter and eddy influences of the outer hooked bar or beach" (155). The narrow outer bar that connects the cliffs of Highland light with the Provincetown peninsula is described as wasting back with the cliffs, and is said to be in danger of breaking through at two points.

H. Mitchell wrote a "Report . . . concerning Nausett beach and the Peninsula of Monomoy" (Rep. U. S. C. S., 1871, pp. 134–143). Monomoy is described as built of sands derived from the bluff of Cape Cod during northeast storms; it grew southward into Nantucket sound at the rate of 157 feet a year from 1856 to 1868. The changes in the beach near Chatham are particularly described. The same author submitted an "Additional report on the changes in the neighborhood of Chatham and Monomoy" (Ibid., 1873, pp. 103–107).

W. Upham published some notes on Cape Cod in the Geology of New Hampshire (1878, III. 300–305), and a more extended essay on "The formation of Cape Cod" a year later (Amer. Nat., 1879, pp. 489–502, 552–565). He described the moraine extending eastward from Sandwich and entering the sea at Orleans (494); north of this point, the Cape consists chiefly of modified drift, rarely containing boulders (537). When the drift plains were deposited, the land stood somewhat higher than at present (561). Provinceland consists of sea sand, supplied by erosion on the east side of the Cape (564).

Chamberlin makes a brief reference to Cape Cod in his essay on the "Terminal moraine of the second glacial epoch." "The great northward hook of Cape Cod is composed of plains and rolling hills of sand and gravel, which resemble accumulations that often accompany the morainic belt on its interior side, and suggest the thought that the hook may be the modified inner border of the moraine which enters the sea near Orleans, and may be presumed to curve northward concentric with the hook, forming thus a loop enclosing the basin of Cape Cod." (Third Ann. Rep., U. S. G. S., 1883, p. 379.)

H. L. Marindin studied the "Encroachment of the sea upon the coast of Cape Cod, Mass." (Rep. U. S. Coast Survey, 1889, pp. 403–407, chart 28). From Highland light to Nauset lights, the average

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recession from 1848 to 1888 was 128 feet, or 3.2 feet per annum. The face of the cliff, whose average height is 50 or 100 feet, has thus lost a total of 30,231,038 cubic yards, or 755,776 cubic yards per annum. The bar south of Nauset, enclosing the north side of Pleasant harbor, extended its length southward some distance in the same period. The same author has made a detailed report on the changes in shore line and anchorage areas of Provincetown harbor in Appendix 8, U. S. Coast Survey report for 1891, with an elaborate chart.

K. Weule has, in his "Beiträge zur Morphologie der Flachküsten" (Kettlers Zeitschr. wiss. Geogr., 1891, VIII. 211–256), discussed Cape Cod at some length (232–238). The tidal currents are regarded as the most important factors in its shaping. A misunderstanding of local conditions is implied when the author asks how "the narrow mainland of uncompacted materials can remain intact in an exposed situation, when even so resistant landmasses as rocky Nantucket and Martha's Vineyard suffer great loss" (232). The present preservation of the Cape is ascribed to the beach sand, brought from the shoals on the southeast by the flood tide. Weule follows Whiting in attributing a greater age to the outer than to the inner side of Provincetown peninsula (234). The existing mainland is regarded as only a remnant of a great extent of drift land (233); this opinion being taken from a report by A. Agassiz.

A brief article of my own, describing "Facetted pebbles on Cape Cod" (Proc. Bost. Soc. Nat. Hist., 1893, XXVI. 166–175), argued from these evidences of æolian action that the plains of gravel and sand were deposited under the air rather than under the sea.

A "Report of the Trustees of public reservations on the subject of the Province Lands" (Mass. Legislature, House, Pub. Doc. 339, Feb., 1893, p. 6) states that "there is evidence that the tides and waves have built one beach after another, each farther north than the last, and that the so called Peaked hill bar is a new beach now in process of formation." The report contains an elaborate map of the sandy peninsula by J. N. McClintock, on a scale of about five inches to a mile, with ten-foot contours. The manner in which the outer beaches overlap the inner ones is very clearly shown. Five photographic illustrations present characteristic views of the dunes.

A general work on coastal forms — "La géographie littorale" — by J. Girard (Paris, 1895), briefly compares Sandy hook and the end of Cape Cod, classifying them with spits formed by littoral currents, but giving no specific description.

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Review of Previous Writings.

The structures of the "mainland" of Truro and of the peninsula of Provinceland are so unlike that their different origins have long been recognized; the former being attributed chiefly to diluvial or glacial and aqueo-glacial agencies, the latter to marine agencies acting on the former. The general character of existing processes by which the shores are undergoing change, and the present rate of action of these processes have been carefully examined by various observers; but no systematic attempt has been made to trace the processes and the changes that they have produced backward to their beginning. This task is therefore attempted here.

Reconstruction of the Original Outline of the Cape.

The development of the existing outline of Cape Cod must be traced backward to the original outline. The initial form that it had before the present cycle of cutting and filling began along its shores may be roughly reconstructed by reversing the marine processes now at work and following them until they lead back through earlier and earlier conditions. The restoration may be regarded as complete, when the reconstructed forms are everywhere of non-marine origin. Then, reversing the order of study, the normal operation of cutting and filling processes should lead forward again to the existing outline of the Cape, and should even allow a reasonable prediction of future changes for some time to come.

Provinceland, the Chatham bars, and Monomoy, and a few small bars near Wellfleet, must first be removed, as they consist wholly of sea-carried materials, their arrangement being closely accordant with action at present sea level. The tidal marshes north of Wellfleet, along Pamet river, and elsewhere, should be excavated. The "mainland," chiefly of glacial and aqueo-glacial deposits, will then stand out alone, as indicated by the outline NBHQPTC, Figure 1. It descends to the shore on nearly all sides in steep cliffs of moderate height; long, straight, or gently curving beaches running along the base of the cliffs. Exceptions to this rule are found almost exclusively on the shores of protected bays, such as those north of Chatham and about Wellfleet. The cliffed descent of the mainland to the smooth beaches is manifestly an indication of destructional retreat from a formerly greater extension seaward, just as the gentle slope of the land to the irregular shore line of the bays is an indication of small change from constructional form.

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Although no close accuracy is to be expected in restoring the seaward extension of the cliffed mainland, there are nevertheless some simple principles that will at least serve to guide us towards a not altogether imaginary reconstruction. First, it must be remembered that general subaerial denudation has not effected significant changes in glacial topography during postglacial time. Second, the restored outline should possess irregularities of pattern comparable to those in the protected bays of to-day, advancing from the headlands and retreating towards the troughs or "valleys" in the high ground. Third, the amount of land restored should be much less on protected shores than on exposed shores. Fourth, cliffs that are now protected by forelands of marsh and bar must not be built out so far that their recession could not have been accomplished before the bars began to grow in front of them.

Possible Changes of Level.

These four guiding principles do not include reference to the effects of change of level, because, if any change has occurred since the time of accumulative construction of the mainland, it has been of small amount, and it has, to my mind, acted on the whole in favor of decreasing the land area by submergence, thus co-operating with the destructive action of the sea. This view is in accord with that expressed by Upham, who thinks that, when the drift was deposited hereabouts, the land stood somewhat higher than at present, and that the numerous small indentations or re-entrants of the shore line, such as occur along the south side of the Cape, are results of a slight submergence of trough-like depressions or valleys. The digitate bays of Martha's Vineyard would seem to lend support to this view; but they are otherwise interpreted by my colleague, Professor Shaler, who regards them as having been formed by subglacial streams acting on sea-floor deposits that had been strewn in front of the ice margin when the sea stood higher than now, although he suspects also that "at the close of the glacial period this region was considerably higher than at present" (Geol. Martha's Vineyard, 7th Ann. Report U. S. Geol. Survey, 1888, pp. 318, 319, 350). The latter view is further supported by the small amount of erosion — about three miles — suffered by the low sandy southern shore of Martha's Vineyard (Ibid., p. 349) since the present level of the land was assumed.

Without undertaking to determine precisely the original level of the Cape mainland, the most plausible explanation of the facts seems to me that the washed gravels and sands correspond to the supermarine

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sandr of Greenland and Alaska; that the troughs, by which the plains of washed sands are trenched, result from the channelling by streams when they carried less waste than while they were previously aggrading the plains; and that the indentations of the shore line are the result of slight depression, whereby the troughs were partly drowned. The reconstruction of what I have above called the "original outline," will therefore not necessarily lead us to the shore line that obtained at the close of the time of accumulative construction, if the land then stood higher than now; but only to a contour line drawn on the original constructional mainland at present sea level. However, between the actual original shore line and the reconstructed contour line, there must have been a difference of degree rather than of kind; the latter embracing a smaller land area than the former, but the general outline and disposition of the land areas probably being of much the same style in both cases, except for the indentations of drowned valleys after submergence. For this reason, no further especial attention will be given to depression in its effect in altering the outline of the Cape.

A proposed reconstruction of the outline of the Cape has been drawn, with the four guiding principles above stated in mind. Trifling additions are made in the bays; none more than 2,000 feet. Significant additions are made on the west side of the Cape; some of these measure 4,000 or 5,000 feet. Two miles or more of land are added on the east side, or "back," facing the broad Atlantic. The margin of the restored outline is indented toward the various troughs and valleys that break the general surface of the mainland. About High head, the northern point of the cliffed mainland, the fourth of the guiding principles comes into play; and hereabouts the most interesting problem of the Cape is found. The view of the peninsula of Provinceland from this commanding point is therefore particularly instructive.

The Problem of High Head.

The cliffed margin of the mainland at High head, H, Figure 1, is notably even both on the northern and western sides. At present, the head is protected both on the west and north by forelands of marsh and bar, the bars springing tangent from cliff fronts farther south or southeast. The bar, Q R, on the west, is part of a long concave shore line, TPQR,—the "west concave" shore,—whose excavated curve is manifestly dependent on the existence of the peninsula of Provinceland to the northwest. Before this concave curve was cut, a nearly straight shore line, CTYQH, — the "west straight" shore, — had been made,

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as indicated by its remnants now seen on the west marginal cliff, QH, of High head, and again about six miles to the south, TC, on Boundbrook, Griffins, and other islands. The cutting of the west straight cliff, QH, must have continued until the peninsula of Provinceland began to project northwest to High head. Then, as the movement of the shore currents was somewhat changed by the interference of the peninsula, the middle of the straight cliff was excavated more rapidly,

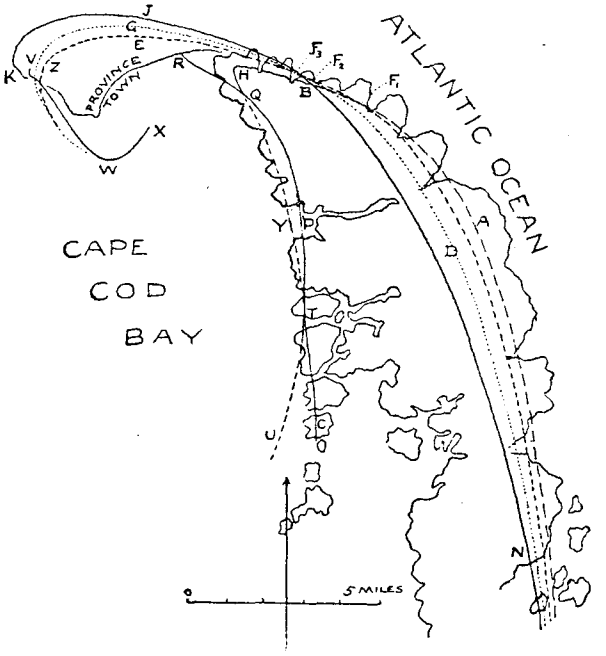

FIG. 1.

forming the west concave shore, TPQ, and the northern part of the straight cliff on High head at the same time came to be protected by the outspringing concave bar, QR, that now encloses East harbor and its marshes on the southwest side.

The bar, BJ, on the north of High head, is part of the long eastern convex shore line, NBJK, whose form is determined by the masterly Atlantic currents. It is along the outer beach of this bar — or of its representative in former days — that the sands of the peninsula have been transported from the southeast; this being the conclusion of all observers, unless perhaps of Hitchcock. Now it follows from the re-

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lation of this northeast bar to the peninsula of Provinceland, and from the relation of the peninsula to the western bar, that a somewhat shorter time was allowed for cutting the north cliff of High head than for cutting its west cliff; but inasmuch as wave energy was greater on the north than on the west, time and energy varied inversely, and hence about the same amount of lost land may be added to each cliff. The amount of reduction suffered on either side of High head is therefore roughly proportional to the time before the bar was built in front of the north cliff.

The north bar, BJ, that for this reason takes our attention, is one of the class built by marine action, as recognized by Admiral Davis. It springs tangent to the curve of the long convex cliff and beach, NB, on the east side or "back" of the Cape. As the retreat of the margin of High head is measured by the time before the north bar was built, the question arises whether bars of this kind are built in front of straight cliffs early or late in the attack made by the sea on the land. This question may be divided into two; the first considering the development of the cliff; the second considering the stage in the development of the cliff when the protecting bar would be likely to grow out in front of it.

Development of Shore Profiles.

Let the activities of the sea be resolved into two components; one acting on and off shore; the other along shore; and let the effects of the first of these components be now examined alone, postponing consideration of the effects of the second component to the next section.

On some young coasts, the on-and-off-shore movements of the sea carry out to deep water all of the waste that is abraded from the land and its submarine slope, leaving the shore line bare.* The rocky floor seen at low tide on the coast of Brittany illustrates this condition. Here the sea is able to do more work than it has to do. Its action is like that of a young river, whose ability to carry load is greater than the resistance of the load that it has to carry, and whose valley floor is therefore attacked and deepened. But as the valley is deepened, the slope, velocity, and carrying power of the river are all decreased; at the same time the load, derived chiefly from the valley slopes, is increased: thus ability to do work gradually falls into

* The problem of flat coasts, with shallow off-shore waters, is so different from the problem here considered that it will be treated independently in a later section.

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equality with the work to be done. When this happy condition is reached, the river may be said to have graded its channel. Youth then passes into adolescence.

A comparable series of changes may be detected in studying the profile of a seacoast at right angles to the general shore line. As the sea can at first usually dispose of more waste than it gathers, the coast is energetically attacked and forced to retreat, and sea cliffs are thus produced. But in virtue of the changes thus brought about, the energy of on-and-off-shore attack decreases, while the waste coming from the growing cliffs increases; thus ability to do work approaches equality with work to be done, and the sea-floor profile, like that of the valley floor, may be said to be graded. When a graded profile is attained, the adolescent stage of shore development is reached.

The amount of retreat necessary before a graded profile is attained varies with the texture of the coast, and with its exposure to the sea. A coast of unconsolidated deposits will soon supply a large amount of waste from its cliffed margin, while the cliffs of a rockbound coast will shed waste slowly; hence, on coasts of given exposure, grade will be assumed with a less amount of cliff-cutting where the rocks are weak than where they are strong. This recalls the behavior of rivers in regions of weak and resistant rocks; in the latter, they may assume gentle slopes; but in the former, rather steep slopes are necessary to carry off the freely offered waste; and gentler slopes can be assumed only as the whole surface is worn down: this general relation having been pointed out some years ago by Major Powell (Uinta Mountains, 194). Moreover, inasmuch as a greater amount of waste can be handled on exposed coasts than on protected coasts, a considerable retreat may develop high cliffs on the former before enough waste is shed from the cliff face to give the shore waves all the work they can do; while on protected coasts a moderate retreat, producing low cliffs, will supply as much waste as can be handled by the sea.

The under-water form of a graded profile, when first developed, also depends largely on the violence of the on-and-off-shore movements of the sea. On a protected coast, the bottom will be degraded so as to descend from the shore line by a gentle slope to an eroded platform of moderate depth; but on an exposed coast, the bottom will be degraded so as to descend from the shore line by steeper slope to a platform of greater depth.

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Typical Shore Profiles.

A graded profile being once attained, its graded condition will be preserved through all the rest of an undisturbed or normal cycle of shore development; shore profiles and river profiles being alike in this as in so many other respects. Before grade is assumed, the ability of the sea may be so far in excess of its load that it undercuts the shore and forms sea caves at tide level, as in profile 1, Figure 2. When grade is first assumed, the coast is usually cut back to a steep cliff, like profile 2. Much later, when the sea has cut back the shore so that the waves must transverse a submarine platform before attacking the land, their strength is thereby so much lessened that the cliff leans back to a moderate slope, as in profiles 3 and 4, and even then supplies enough waste to keep the waves at its foot fully occupied.

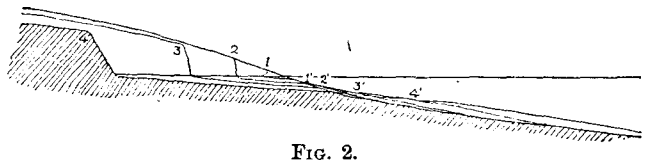

Fig. 2.

There is something more than analogy in the comparison that may be drawn between the longitudinal profile of a stream and the transverse profile of a shore. In youth, each usually has its torrent or upper portion, where ability to carry load is greater than load to be carried; but as development progresses, the graded condition of mid-stream extends headward, and after a time reaches all the way to the headwaters. At the same time, the lower or floodplain-delta portion extends seaward, its grade being rather steeper in adolescence, when much material is brought from the headwaters, than later, in maturity and old age, when the supply of waste is very slow. The critical point, where marine action changes from degrading the near-shore bottom to aggrading the off-shore bottom, migrates seaward, as 1′, 2′, 3′, 4′, in Figure 2. At the same time, the seaward extension of the bottom deposits increases. Furthermore, the comparison between stream and sea suggests the need of examining that process on the sea floor, which corresponds to corrasion in the stream bed. Sea-shore profiles make it clear that a considerable deepening is accomplished on the floor of the platform, landward from the critical points, 1′, 2′, etc. Off the eastern cliff of Cape Cod, this deepening can hardly have been less than fifteen or twenty fathoms: off the Chalk cliffs of Normandy, a similar scouring and deepening of the bottom may be inferred. We

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are accustomed to study transportation and deposition as submarine processes, but little attention has been given to decomposition, disintegration, corrasion, or any other process by which the sea floor is degraded. The subject deserves careful investigation.

It is manifest from the preceding paragraphs that a graded profile may be attained much earlier on one part of a shore line than on another; for the texture, the original profile, and the exposure of a coast all vary from place to place. But in a region like Cape Cod, where the original shore line consisted wholly of uncompacted materials, this aspect of the problem need not be considered further.

Development of Shore Outlines.

It is not, however, only in on-and-off-shore action that a close comparison may be drawn between the operations of marine and fluviatile agencies. The 'long-shore action of the sea also is in many respects comparable to the down-stream action of rivers. Beginning on an unevenly deformed land surface in a region of moderate rainfall, where there are many heights and hollows, the drainage will at first consist of many small independent systems, each one transporting waste from the initial divides down the initial slopes into the initial hollows. Every stream proceeds, by degrading and aggrading its course, to develop a line of slope on which its ability to do work shall everywhere equal the work that it has to do. As the eminences are worn down and the hollows are filled up, local systems that were at first independent become confluent, and the drainage of the higher ones is discharged to the lower ones. Every change of this kind will call for rearrangement of the degraded and aggraded slopes in the confluent basins. Ultimately, all the separate systems will, in one combination or another, find outlet to the sea, and the waste will be carried a long distance from the main divides to the main river deltas.

It is much the same with the action of the sea. Leaving the on-and-off-shore action out of consideration for the moment, let us view only the 'long-shore action, as determined by the dominant rather than by the prevailing movements of the littoral waters. The projections or headlands of the constructional shore line act as so many divides, on either side of which the 'long-shore currents flow away from the apex, as in the uppermost outline in Figure 3. The re-entrants or bays are so many basins into which the 'long-shore currents converge from the adjacent headlands. The headlands are slowly worn back, and the waste is carried along their sides into the bays, where it forms aggrading

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pocket beaches or bridging bars, as in the second and later outlines of Figure 3. The initial irregularity of shore outline is thus replaced by a graded outline; grade being first attained in the bays, and last on the headlands, much as was the case with stream action. As the headlands are cut farther back and beaches are formed at the base of their cliffs, then the 'long-shore action is more and more thrown into one direction or the other from the chief headlands, transportation is carried on past many of the subordinate headlands, and much of the waste finds its way into the chief re-entrants of the shore line, as in the lowermost outline of Figure 3. We should expect to find

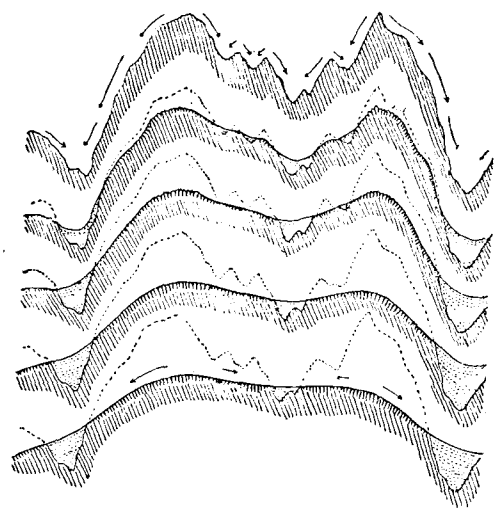

FIG. 3.

inside the long-sweeping curve of the aggrading shore line of the chief bays more or less distinct record of the sharp-curved pocket beaches of an earlier stage.

However irregular the initial shore line was originally, and however many divisions were then made in the direction of the 'long-shore currents, the time will come when only a few of the most prominent and resistant headlands survive, as in the later outlines of Figure 3; elsewhere the 'long-shore action is developed into a continuous movement. Truly the direction of transportation along the graded shore line is sometimes one way, sometimes the other, according to the sweep of storm winds; but if the dominant currents alone are considered, the movement is essentially constant. The graded condition,

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first reached on the pocket beaches, comes to prevail all along the shore; ability to do the work of transportation is everywhere equal to the work of transportation to be done.

In the river problem, the number of independent river systems that occupy the originally deformed surface varies with the strength of the initial relief and with the rainfall. A light rainfall and a strong, rapid-growing initial relief of resistant rocks produce many independent river systems, and a long time must elapse before a general grade is attained. The early stage of this condition is illustrated in the lava-block mountains of southern Oregon, so well described by Russell (4th Ann. Report U. S. Geol. Survey, 435). But a heavy rainfall and a faint, slow-growing initial relief of weak materials may allow the immediate development of a single river system, soon attaining grade over the whole area concerned. So with the sea. Moderate 'long-shore action and strong initial irregularity of resistant rocks break up the 'long-shore currents into many systems at first; the grading of the shore line and the union of the many currents can be accomplished only after a long time of endeavor. But strong 'long-shore action and moderate initial irregularity of weak materials may permit continuous 'long-shore movements for a long distance on well graded beaches almost from the very first.

Both in valleys and on coasts — in rivers and on shores — the graded condition will be reached sooner on certain stretches than on others; and just as an alternation of rough rapids and smooth-flowing reaches indicates a youthful stage of river life, so an alternation of ragged headlands and smooth-beached bars indicates a youthful stage of shore line development. But in time even the more resistant parts will be trimmed off so as to accord with the less resistant, and then down-stream transportation — or 'long-shore movement — is well developed; the adolescent stage is reached. From this time forward, on a shore as in a river, the grade is normally changed only where and when a change of load calls for readjustment; the readjustment necessitating an aggradation or degradation of the valley floor, or an advance or retreat of the shore line, as the load may increase or decrease.

It should of course be understood that comparisons of this kind are not formal comparisons in which the condition of one member may be inferred immediately from those of its analogue. The purpose of the comparison is not to compel explanation, but chiefly to borrow illustration of the systematic processes of land sculpture from the better known examples of river action, and apply them to the less studied examples of shore action; less studied certainly in this country,

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where our great interior areas have for some decades past absorbed the attention of geologists; more studied than river action in Great Britain, but not from the point of view here taken.

Under favorable conditions, irregular shore lines may be smoothly graded early in their cycle of development. This is well illustrated in the case of Martha's Vineyard. Here an extremely irregular constructional shore has been reduced to a remarkably even and well graded outline in a relatively early stage of the attack of the sea on the land; for although a matter of two or three miles of the southern headlands of the island have probably been cut away by the sea,* a good part of the original shore line still remains in the branching bays behind the bridging bars. The straight-cliffed headlands stand perfectly in line with the bars across the bays. The later stages of outline on graded shores are considered in the third section below.

Application of the Foregoing to Cape Cod.

The foregoing account of the development of shore lines is perhaps an overlong preparation for the application of the simple principles that govern shore changes to the case of Cape Cod; but the excuse for the details into which I have entered is the desire to show good ground for the conclusion which they support; namely, that on a coast as weak as the mainland of Cape Cod, any originally irregular shore line would soon be reduced to grade by the action of a sea so energetic as the Atlantic, with its frequent southeast and northeast storms. Only a moderate time and a moderate recession is therefore necessary for the production of the even northeast cliff of High head. It does not, however, follow from this that only a short time actually elapsed in this work, for as far as has yet been stated, the High head cliff that we see may have been cut far back from the first position of an even cliff on this part of the coast line. Whether the time was long or short can be best determined by examining into the conditions which determine the development of the bar by which the cliff is now protected, this being the second problem announced above.

It should be noted that when the northeast cliff of High head formed the open shore line of this part of the Cape, the outline must have extended in a sympathetic curve, HBF_1A, for some distance southeast of its present limit; and from this early form there must have been a gradual change to the shore line of to-day. At some time during this change, the protecting bar, BJ, must have been built out

* Shaler, *loc. cit.*, 349.

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to the northwest. The problem is to determine at what stage in the history of a cliffed shore line such a bar or spit might grow out from one part of its face and protect another part.

Off-shore Bars.

In order to avoid misapprehension, it is advisable to make careful distinction between those bars or spits which spring as tangent attachments to a cliffed shore, often extending into comparatively deep water, and those off-shore bars which are built up from the bottom in shallow water, not immediately connected with the mainland. Exam-

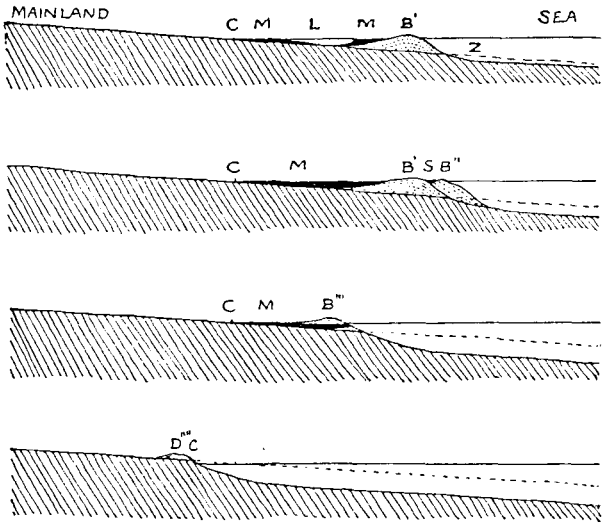

Fig. 4.

ples of the latter class are common along a great extent of our southern coast, especially where the tides are weak. Briefly stated, their history seems to be as follows. When waves roll in upon a shelving shore, as in Figure 4, much of their energy is expended on the bottom. Between the line of their first action far off shore and their final exhaustion on the coast, C, there must be somewhere a zone of maximum action. This zone must lie farther seaward when large storm waves roll in than when the sea is slightly ruffled in fair weather. Let the zone of maximum action for storm waves be shown by Z in profile. Here the bottom is deepened; the coarser particles are moved landward, forming a shoal and in time a bar, B′, enclosing a lagoon, L; while

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the finer particles are moved seaward, beyond the limits of Figure 3, where they are distributed in moderate thickness over a considerable area. During this process, we may imagine the storm waves to say: "We cannot to advantage attack a coast where the off-shore water shoals so gradually; let us therefore first deepen the off-shore bottom, so that we may afterwards make better attack on the coast." So saying, a preliminary off-shore bar is built up by the storm waves in position B′; and afterwards, at times of exceptional storms, successive additions may be made on its outer side, as B″. Wind action builds the bar up with dunes, and carries much sand over into the lagoon. But a time will come when the bottom farther to seaward has been deepened enough to enable even the greatest waves to act severely on the outer slope of the bar, taking from it more than they bring to it; then the outward advance of the bar is changed to a landward retreat, and it is pushed back to such a position as B‴. This change in behavior may be taken to separate the stages of youth and adolescence in the development of a shore line of this kind.

Young bars that are advancing or that have advanced seaward may often be recognized by belts of dunes, B′, B″, roughly parallel to the shore, enclosing lines of marsh or "slashes," S, as they are called on the coast of New Jersey. Adolescent bars, retreating landward like B‴, may be distinguished by the exposure of the dark mud of the lagoon marsh, M, on their outer slope, as is sufficiently explained by the diagrams. Many examples of this kind might be cited. In time, the retreat of the bar will carry it back to the mainland; then, as long as the marginal cliff is not too high, the dunes, D⁗, will be heaped directly on the land slope, and the mature stage of shore development is reached. In this stage, the depth of water near the shore is much greater than it was originally; degradation of the sea floor reaching to depths much below low tide.

An interesting variation on this type of coastal forms is found on coasts whose submarine slope varies, so that off-shore bars are formed in one district, but an immediate attack is made on the land in a neighboring district. The coast of New Jersey gives a standard example of this kind. About Atlantic city the bars are built off shore; about Long Branch, the land is cut back in a retreating cliff of moderate height. Although now generally retreating and exposing marsh mud on their ocean side (Ann. Report N. J. Geol. Survey, 1885, p. 80 *et seq.*), the bars frequently possess dune ridges and slashes, as if they had once advanced seaward. Somewhere in the earlier history of this coast, there must have been a point or fulcrum of no advance

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or retreat between the advancing bars and the retreating cliff. It should not be overlooked that 'long-shore action has a share, often a large share, in the development of compound forms of this kind; but it is quite conceivable that they might be developed essentially under the control of on-and-off-shore action alone. A second example of this kind is perhaps to be found in the combination of the bars from Chatham to Nauset with the cliffed margin of the Cape mainland farther north; but into this problem it is not desirable to enter further at present. The origin of tangent bars or spits, built out into comparatively deep water, may now be taken up.

Tangent Bars or Spits.

In order to understand more clearly the conditions under which tangent bars would form, it is necessary to return for a few moments to the problem of the varying outline of a graded shore as dependent on an increase of load. It is advisable to enter this phase of the problem through comparison again with the development of rivers and valleys.

In the case of adolescent rivers, the increasing dissection of the drainage basin by growing headwater branches may frequently cause the load to continue to increase after the first attainment of a graded slope along the trunk river. As a consequence, the trunk river must aggrade the valley floor, forming a flood plain, until the load begins to decrease later on in maturity. Much in the same way, 'long-shore action of the sea on a coast of graded outline may gather an increasing load as the cliffs retreat and become longer and higher; and with this increase of load, certain parts of an early-graded outline may have to be built forward into the sea. But on pursuing this comparison a step further we find here, as in some earlier cases, a contrast replacing the agreement thus far traced between the river and the 'long-shore action. Not only the load, but also the volume of a river increases from youth to maturity by reason of the better development of stream lines all over the drainage basin; and this increase of volume tends to prevent the aggradation asked for by the increase of load. Similarly, the volume of water involved in the 'long-shore movements becomes greater as the inequalities of a young shore line are reduced to the smooth curves of adolescence and maturity; but here the increase of volume causes the shore waters to move in curves of larger radius than before, and this change may require the beaches to grow forward on certain concave or incurved parts of the shore line. In such case, increase in the volume of 'long-shore water movements may co-operate with the

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increase of load in tending to build the land out into the sea. Here rivers and 'long-shore currents have unlike behavior.

One of the best examples of this kind that has come to my notice is found on the coast of Georgia and Florida, where the better adjustment of coastal bars to shore currents and the consequent increase in volume and strength of the latter seems to have led to the out-building of the several bars that are involved in the southward migration of Cape Canaveral.* The accompanying digaram, Figure 5, illustrates the essential features of the changes here inferred. The general attack that is at first made nearly all along the ragged coast soon comes to be resolved into two diverse actions; a persistent attack on the chief medial headlands, while the subordinate headlands are protected by the growth of off-shore bars. Let the ragged outline of Figure 5 represent the original shore line of an uncompacted land mass. The general attack by the sea first cuts off all the headlands, forming cliffs 2, 3, more or less connected by bars. When longer and higher cliffs, 4, are developed, they supply so large an amount of waste and allow the movement of so large a volume of water along shore that the less exposed cliff of earlier intention in the upper part of the figure is no longer attacked, but is protected by a spit, 4′, that springs out from the main cliff, prolonging its curve in one direction or the other, — here, upward, — according as the tides and the on-shore winds determine the direction of the 'long-shore movement. In this case, on-and-off-shore action and depth of water have little to say. Wherever the dominant 'long-shore movement advances, there the tangent bar must grow, whether the water is shallow or deep.

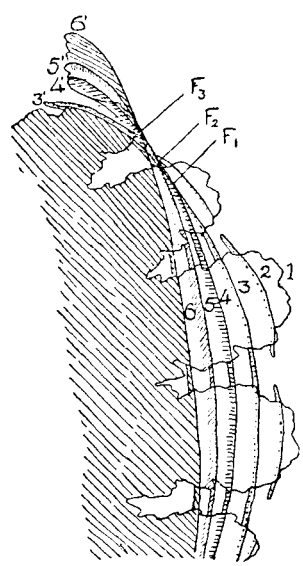

FIG. 5.

* This peculiar change in the situation of the cuspate foreland known as Cape Canaveral was briefly stated by the writer in Science, 1895, I. 606. It has later been found that Weule had previously noted the fact of migration (*loc. cit.*, p. 253), although not mentioning the cause here suggested to account for it.

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Illustration from the Coast of New Jersey.

An example suitable for illustration of this case is found in the relation of Sandy hook to the Long Branch cliffs on the New Jersey coast, as exhibited on the excellent topographical maps of that State. Although now protected by the spit of Sandy hook, both Rumsor neck and the Highlands of Navesink are truncated by sea cliffs. The truncation must have been accomplished before the spit was built, and therefore before the Long Branch cliff had been pushed back to its present position. Stage 3, Figure 5, essentially represents this relation. In the change from earlier stages to the present, the 'long-shore action has increased in consequence of the general smoothing of the outline, and the direction of 'long-shore movement has been somewhat changed; so that now instead of carrying the waste from the Long Branch cliff directly to the truncated headlands next north, it is carried along an independent path forming the spit of Sandy hook outside of the line of truncation. It is interesting to notice that the Long Branch cliffs were evenly graded, and that the spit was formed rather early in the general attack of the sea on the land hereabouts, and that a very slight change in the outline of the chief cliff sufficed to cause the growth of the spit outside of the subordinate cliffs further north. The various fluctuations in the growth of the spit and the intermittent destruction of its slender bar are described in the Annual Report of the New Jersey Geological Survey for 1885, p. 78.

The Long Branch cliff has for some time been retreating under the blows of the Atlantic breakers. The farther it retreats the longer the stretch of cliff becomes; it is undoubtedly much longer now than formerly. It may be fairly inferred that the two great spits, to the south as well as to the north of the cliff, have always been, as now, essentially tangent to the cliff front. It follows necessarily that the point of the attachment of the spits to the mainland has shifted, and that the spits have also been pushed backward at equal pace with the retreat of the cliff. With these conclusions in mind, the problem of High head and the northeast bar may at last be taken up.

Growth of the Provincelands.

There is good reason to think that the analogy between Sandy hook and the Provincelands pointed out by Admiral Davis may be carried much further than he suspected. The great convex cliff line on the back of the Cape corresponds to the slightly convex line of the Long Branch cliff; the northeast cliff of High head is the counterpart

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of the protected cliff of the Navesink highlands; the slender bar that springs tangent to the curve of the back of the Cape and runs to the broad peninsula of the Provincelands is essentially a repetition of the slender bar that springs north from the Long Branch cliff and runs to the broadened peninsula of Sandy hook. The point where the bar now springs northwestward from the long convex back of the Cape is not the point where the bar first began to grow. Its original point of attachment must have been southeast of the present point; and in the change from the original to the present arrangement, both the cliff and the slender bar must have been forced back, in the very manner already described for the example in New Jersey. Marindin's report gives precise data for the retreat of the cliff; and the story of the buried canoe, recorded by Thoreau, gives support to the retreat of the bar near its point of attachment. In both examples, the farther part of the great spit has grown by addition to its seaward side in order to keep the outline in a curve sympathetic with the retreating cliff; the outward or eastward growth of Sandy hook being described in the Annual Report of the New Jersey Geological Survey for 1885, p. 77; the similar growth of the Provincelands is more fully stated below. As a result of the outward growth of the spit while the cliff is retreating, there must be a neutral point or fulcrum of no change somewhere on the connecting bar: and with the further straightening of the cliff front, the position of this fulcrum must generally shift toward the spit, as shown by F_1, F_2, F_3. Figure 5.

The original point of attachment of the connecting bar on Cape Cod must have been at the intersection of two converging lines determined by the northeast cliff of High head and the innermost or oldest of the bars in the Provinceland peninsula. The first of these lines is well defined, HB, Figure 6; the second is less distinct, but appears to be recorded in a sand bar on the line EF_2. The form of this bar has probably been somewhat changed by wind action; yet the trend of its inner margin along the shore of East harbor is comparatively straight, as if it had not been much altered from the form given when it was built. Its trend departs slightly from the direction of the adjacent Atlantic shore, as if had been determined by conditions now vanished.

The intersection of the two guide lines, HB and EF_2, when prolonged to the east-southeast, is found at a point F_1, about 4,000 feet off the present shore, and about a mile and two thirds east-southeast from the present point of attachment of the springing bar. Judging by the present rate of retreat of the cliff line, this outer position must have been occupied about 1,200 years ago. These figures are of neces-

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sity only approximate, but they are believed to give a fair indication of the order of magnitudes involved, both in space and time. We may then infer that when the general outline of the back of the Cape had assumed the position of the line AF_1BH, the shore was well enough graded to supply material for the building of a spit; and that the curvature of the shore at the point F_1, assigned for the beginning of the spit, was such that the dominant 'long-shore currents, moving from south to north in flood tide or under southeast storms could no longer

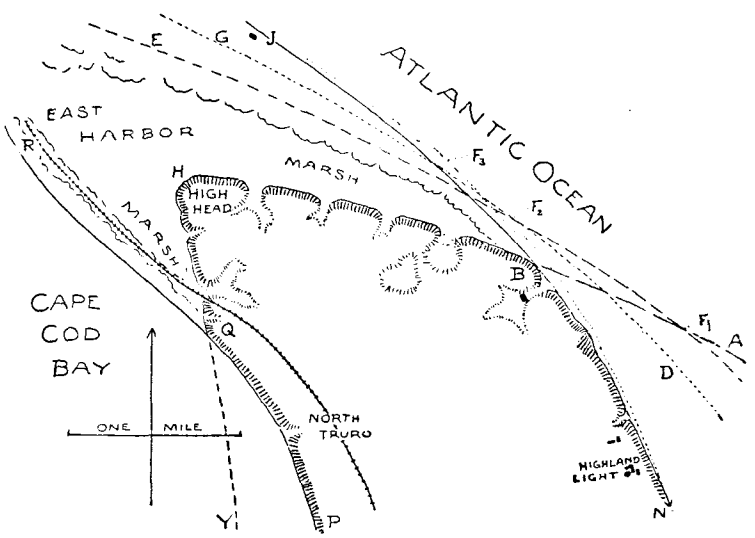

FIG. 6.

follow the shore, but departed from it outwardly by a small angle. Thus the protecting bar, F_1E, began to grow in front of the High head cliff.

At an earlier stage the 'long-shore currents must have been much interrupted by the irregularities of the original shore line. No large and well developed current could at that time follow these irregularities. But as the headlands were cut back and the bays bridged across, and the shore assumed the outline ABH, then the resistance to the development of the current became less and less; thereby the current became stronger and stronger, and desired a straighter and straighter path for its movement. At the same time, a greater and greater volume of waste was supplied from the growing cliffs. As long as the back of the Cape projected farther into the sea than

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now, the northward shore current may have swung pretty well around the mainland, as sketched in line ABH. But as the east side of the Cape was cut away and straightened, and as the shore current grew stronger and stronger, it became increasingly difficult for the waters to turn the curve that led to High head; and at last, when the turning was impossible, the spit began to form on the line F_1E. As the change progresses, the current swings on a fulcrum, F_2; the spit broadens by the external addition of new bars, F_2G, as well as by the formation of sand dunes inside of the curve; and the fulcrum shifts along the shore to the northwest, as indicated by the points F_2, F_3, Figure 6, in the manner already explained for Figure 5.

The important point to note is that here, just as on the New Jersey coast, the grading of the initial irregular shore line into a curved cliff shore, and the straightening of the curved cliff shore enough to require the growth of the tangent bar, must have been accomplished early in the development of so weak a land mass as Cape Cod in face of waves so strong as those of the Atlantic.

Dimensions of the Original Cape.

Now inasmuch as no very long time can have been required for the Atlantic waves to wear back the original shore line of the Cape to a graded outline, ABH, of which the High head cliff is a part, and inasmuch as the growth of the springing spit must have been begun soon after the grading of the shore, it follows that the original constructional outline of the land in front of the High head cliff cannot have extended far into the sea. I have given it an extension of 3,000 feet in Figure 1. A similar original extension of all the mainland of the Cape may be assumed outside of the graded shore line ABH, that existed before the springing spit was formed; and thus the original outline of the eastern side of the mainland has been roughly sketched in. As drawn in Figure 1, the greatest retreat from the original shore to the present shore is nearly two and a half miles, and at the present strength of wave action, 3,000 or 4,000 years may be roughly taken to have sufficed for the accomplishment of this change. This time is probably too long rather than too short, for the retreat now must be slower than when the cliff was lower.

It should be carefully understood that the period here computed does not measure postglacial time; for, as already stated, it is believed that the land hereabouts stood somewhat higher than now during the accumulation of the stratified sands, and that only after the time of

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accumulation were the valleys and low grounds slightly submerged by a moderate depression of the land, and the work whose duration is here computed begun. The time that passed while the sea was at work on some lower shore is not measured. There is no indication of a recent elevation of the land hereabouts, as far as the shore features testify: even the protected cliffs of High head are cut down to present sea level.

The Nauset bar extends southward from the cliff at the point N. The earlier positions were prolongations of the lines A, D. The point of attachment must therefore have migrated to the southwest; the retreat of the cliff front determining the retreat of the bar that stands in line with it. How the problematic islands off Chatham affected the behavior of the bar is not here inquired into.

Inasmuch as the recession of the eastern shore is believed to have been of moderate measure, the loss on the western shore must have been still less. This is considered in a later section.

The Origin of Race Point.

Two important consequences follow from the swinging of the shore current on its movable fulcrum. The first gives explanation of the overlapping of the newer shore lines outside of the older body of the peninsula, as stated in the Report of the Land and Harbor Commissioners, quoted above. This is only a repetition of the process by which the spit first departed from the beach on the back of the Cape itself. The outer margin of the Provinceland peninsula is therefore its very youngest part, and not its oldest, as supposed by Whiting. The long bar, F$_5$JK, ending in Race point, is a distinct external addition to the older body of the Provincelands, and a long narrow "slash" is included behind it. It has grown out into comparatively deep water, for the 20-fathom line lies only 1,700 feet off shore to the northwest. Peaked hill bar may be, as the Commissioners have plausibly suggested, the embryo of still another external bar.

It may be noted that small spits departing tangentially from curved beaches are not uncommon. The map accompanying Whiting's report shows two of them near Wood End, one pointing east, the other north, from the sharp curve of the bar, as if determined by a strong southwest storm, whose waves worked eastward and northward from the apex of the curve at Wood End. A minute spit of this kind is shown on the chart of Cape Cod bay (Coast chart 110, printed 1890), a little northeast of Race point; but a later edition of the chart (1892) carries a smooth curve around the point. Small examples of these

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forms. trending eastward, were seen on the south shore near Long point light, at the time of my visit to the Cape last summer.

The Wasting Shore from Race Point to Wood End.

The second consequence of the outward deflection of the current around the peninsula is the rapid consumption of the bar, VW, that extends south from Race point inlet to Wood End, the long "finger" at the end of the Cape. This suggests a preliminary digression. Wonder is often expressed at the ability of sand bars to withstand the violence of the surf that breaks unceasingly upon them. The sands are entirely unconsolidated, and their surface layers are moved by every surge of the waters. Yet the form of the bar changes very slowly. The reason for this must be found in the continual feeding, from the cliffs and from the bottom off shore, by which the volume of the bars is sustained. The bars of our southern Atlantic coast presumably receive much of their sand from the bottom. Sandy hook receives much of its supply from the retreating cliffs at Long Branch. If the supply be withheld, the bar will be rapidly swept away. It may not be that the grains of sand are actually ground to dust, but that they are brushed along, and when no followers come to take their place, it is left vacant, and the face of the bar retreats; its dunes are cut back, and a low cliff-shore is formed.

As long as the outside of the peninsula formed a continuous curve, sand was carried along it in plenty from the cliff and the sea floor on the back of the Cape, and probably also from the shoals where Webbs island and its vanished mates once stood off Chatham. This condition is represented in line DGVW. But as the cliff from Nauset to Highland was cut farther back, and the shore current became unable to follow its earlier path along the margin of the peninsula, the additional bar, ending in Race point, was laid out, and the long marshy "slash" was enclosed behind it. From the beginning of this additional bar until the present time, the supply of sand carried around the western curve of the peninsula was greatly reduced; at times it may have ceased entirely. The supply being thus reduced or cut off, the bar southward from Race point inlet nearly to Wood End rapidly wasted; and the sand taken from it by northwest gales went to supply the correspondingly rapid growth of Long point, WX, into Provincetown harbor, which Whiting shows to have extended many feet eastward in the fifty years past. Like Race point, Long point has advanced into comparatively deep water; the 20-fathom curve lies only 600 feet off shore; the same depth is not found for almost three miles off the cliffed shore of the "back" of the Cape.

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The Western Side of the Cape.

The western side of the Cape offers simpler problems than those of the eastern side. The first task here attempted by the waves was the development of the long west straight shore line, HQTC, of which only the extremities now remain. This does not seem to have required anywhere a greater recession than 3,000 feet. It must have been accomplished chiefly by northwest gales and north-to-south shore currents, by which the waste gathered from the more continuously cliffed shore was carried southward to tie together the several islands below South Truro. If southwest gales and south-to-north shore currents had been dominant, an acuminate spit should have been formed in prolongation of High head, where the waste would have been supplied from both sides of the Cape; but of this there is no sign.

The modification of the west straight shore line by the excavation of the present concave shore line, QPT, undoubtedly results, as has already been stated, from the disturbance of antecedent conditions that was caused by the growth of the Provincelands to the northwest. The northwest gales gradually came to have less and less influence; for some time past, they must have ceased to be dominant; the chief control of shore movements now seems to be in the hand of the weaker southwest gales; for both the offsetting spit at the mouth of Pamet river, P, and the outspringing bar, QR, that protects High head on the west, imply a northward transportation of sands. Some southward movement, however, still occurs, as might be expected; for at the faint angle, T, where the older straight shore line, HQTC, is now cut by the concave shore line, QPT, a spit projecting to the southwest seems to have been begun, and its continuation under water is indicated by a shoal of sympathetic curvature, TC, some five and a half miles in length. How far this shoal may be a new feature, originating with the excavation of the concave shore line, or how far it may be of much greater age, dependent on the extensive Billingsgate shoals, where outlying islands are thought to have originally stood, is for the present an undecided question.

Protection of Provincetown Harbor.

A matter of considerable economic importance turns on the changes experienced by the "wrist" of the Cape, the narrowest part of the bar that connects the mainland or "forearm" of the Cape with the peninsula or "hand." The people of Provincetown feel anxiety lest the sea should breach the bar and wash a great amount of sand west-

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ward past High head into their excellent harbor. The records of changes in the bar that connects Sandy hook with the Long Branch cliffs give ground for this anxiety. The point that I wish here to call attention to is that the only part of the northeast shore that is liable to be broken through lies on the stretch, BF_3, between the point where the connecting bar springs northwest from the great cliff and the point where the "fulcrum" is at present located. Within this stretch, the bar is generally retreating, being cut on the outer side, and reconstructed on the inner side.

Two safeguards may be suggested. One would cause the fulcrum to migrate southeastward, thus diminishing the length of the narrow and breakable bar, and at the same time increasing its breadth and strength. This would be accomplished by the construction of bulkheads along the outside of the narrow bar, or wrist, so as to catch the drifting sand instead of allowing it to pass by; thus the bar might be broadened and strengthened. Judging by the rapidity with which the body of a wrecked vessel causes an accumulation of sand on its southeastern side, a significant addition to the narrow bar might soon be made in this manner. Manifestly, the greatest economy in the use of the drifting sand requires that the bulkheads should be continually built out so as always to project a little beyond the aggrading shore line. There are indications that this very result is at present being accomplished by natural process, for the beach in the narrow stretch, BF_3, is now notably broadened in front of its former line at the base of the surmounting dunes.

A more economical and enduring protection of Provincetown harbor than the above plan suggests has been already secured by completing the extremity of the bar, QR, that some years ago almost enclosed East harbor; so that if storm waves should temporarily breach the narrow connecting bar on the ocean side, — the "wrist" of the "hand" of Provincetown at the end of the "bended arm of Massachusetts," — all the sand that was carried through the breach would settle in East harbor, and thereby strengthen the embankment against further encroachments. A second protecting dike has been built across the marsh, northeastward from near High head. The fear that, in case the narrow connecting bar or "wrist" should be breached, the whole action of the Atlantic 'long-shore currents would thereafter be directed through the breach into Provincetown harbor, is groundless. The whole history of the growth of the peninsula demonstrates that the 'long-shore currents must continue to swing in long curves of large radius in the future, as in the past.

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The danger of silting up the Provincetown harbor by drift coming from the west concave shore line along the west protecting bar of High head does not appear to be imminent, for the processes of transportation are comparatively slow on the inner side of the Cape; but the danger is nevertheless real, and nothing but an extensive and expensive system of bulkheads from North Truro northward, on the stretch PQ, appears to be sufficient to avert it.

The destruction of the narrow strip of sand-bar shore, VW, between Race point and Wood End seems to me to threaten Provincetown harbor with a greater danger than any that it is exposed to from the east. This shore is now wasting rapidly. Once broken through,* the currents driven by northwest gales, as well as by the rising tide, would no longer have to swing around Wood End, W, and deliver their load of drifting sand to Long point, X; they would in all probability invade the harbor directly, cutting away the low-tide flats that now expand south of the village, and throwing the detritus thus gained into the harbor. Attention has been called to this danger by Marindin in the Coast Survey report for 1891, Appendix 8. While bulkheads may delay the destruction of the narrow bar, they can hardly preserve it even through a brief historical period. It has been proposed to abandon the wasting bar to its fate, and to protect the harbor by building a dike from the west end of the village across the flats to Wood End. A partial protection might be gained by building bulkheads on the northern shore of the peninsula, two or three miles east of Race point, K. Drifting sand from the east would then be stopped there. Race point, no longer so well supplied with sand as now, would be wasted by the northwest storms, and the sands carried from it would go southward to repair the shore towards Wood End. The protection of the bar northeast of High head near F_3 would, to a certain extent, work in the same direction by diminishing the supply of sand for the Race point bar; but a considerable time might elapse before any advantageous effect from this cause would be felt.

The Future of the Cape.

The encroachment of the sea on the back of the Cape is undoubtedly destined to continue until the Truro mainland is all consumed north of Orleans, the "elbow" of the bended arm. At the present rate of recession — 3.2 feet a year — eight or ten thousand years will be required for this task; and this without considering the aid given by the

* A small breach has been made in this bar during the past winter, as I have learned from a recent visit to Provincetown.

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waves of Cape Cod bay, whose concave sweep along the Truro shore shows their competence to do no insignificant share of the work.

It does not seem at all likely that, while the rest of the Truro mainland is wearing away, the spit at Race point will of itself curve around to the south, and thus save from destruction the narrowing bar which encloses Provincetown harbor on the west. A great volume of transported sand would be needed to continue the bar in the deep water through which its present curve would lead. Moreover, the shoal known as Peaked hill bar may, as has been suggested, mark the beginning of a shore line exterior to that of the present Race point curve. It is possible that as additional tangent spits are lapped on the outside of the curve, Race point will be cut back by a current from the northwest, working opposite to the great current that rounds the peninsula from the east; a cuspate or acuminate spit being then formed in the angle between the two, such as now exists at Great point, Nantucket. There, the transportation of shore waste is northward on the east shore and southward on the west shore, according to the memoir by Admiral Davis; this being proved by the drift of coal and bricks from vessels wrecked on the east shore (*op. cit.*, 139). The occurrence of these "cuspate forelands," as Gulliver has called them (Bull. Geol. Soc. Amer., 1896, VII.), is not so much of a rarity in nature as might be imagined from the little that appears about them in books; their growth being sometimes attributable to accordant currents that flow towards the point on either side; sometimes to opposing currents, one flowing inwards, the other outwards. Good reasons have been given by Abbe for believing that Cape Hatteras and the other cuspate capes of the Carolina coast have been built between opposing currents (Proc. Bost. Soc. Nat. Hist., 1895, XXVI. 489).

The Provincetown peninsula may be expected to outlast the Truro mainland; for as long as the latter exists, the former must receive contributions from it. But when the mainland is washed away, — ten thousand years hence, at the present rate of wearing, — then Provinceland must rapidly disappear. Sable island, a long sand bar off Nova Scotia, is perhaps to be regarded as the vanishing remnant of a destroyed drift island (see Trans. Roy. Soc. Canada, 1894, XII. pt. 2, pp. 3–48; also, note in Science, 1895. II. 886). It may in this sense be taken to represent a future stage in the destruction of Cape Cod. All these changes are rapid, as changes go on the earth's surface. The Truro mainland will soon be destroyed, and the sands of Provinceland will be swept away as the oceanic curtain falls on this little one-act geographical drama.

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XVII.

CONTRIBUTIONS FROM THE ZOÖLOGICAL LABORATORY OF THE MUSEUM OF COMPARATIVE ZOÖLOGY AT HARVARD COLLEGE, UNDER THE DIRECTION OF E. L. MARK, LXIV.

PRELIMINARY NOTES ON THE EMBRYOLOGY OF THE STARFISH (ASTERIAS PALLIDA).

By Seitaro Goto.

Presented by E. L. Mark, April 8, 1896.

In this preliminary notice I propose to give a brief account of the principal results of the study which I have been carrying on during the past winter. Since I began my study, two papers in the "Quarterly Journal of Microscopical Science," covering the same ground in other species, have come to my notice, one by Bury, and the other by MacBride. But as the results of these observers are at variance on some important points, it will, I believe, not be without interest to publish my own, which, it will be seen, are mostly, but not altogether, confirmations of those of MacBride.

The material was collected last summer in Mr. Agassiz's Laboratory at Newport, R. I., where I was enabled to work for several weeks through the courtesy of the owner, to whom my best thanks are due. It will be observed that I have studied the same species as that on which Mr. Agassiz himself worked about thirty years ago, — a species which in the course of its development passes through typical Bipinnaria and Brachiolaria stages.

(1) A few words as to the orientation of the body. In the Brachiolaria stage the sagittal plane of the body passes through the dorsal Brachiolaria arm, and is at right angles to the line joining the tips of the other two arms. It also passes through the anus and the middle of the mouth. In later stages, as metamorphosis approaches more and more its end, the anus shifts its position considerably, and the sagittal plane can be determined externally only by means of the Brachiolaria arms. I find the plane determined by this means constant for all practical purposes; that is to say, it bisects the stomach as well as the body as a whole, and passes through both the dorsal pore and the point where

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the definitive mouth is formed. As the Brachiolaria arms are visible until a very late stage of metamorphosis, this method of determining the principal plane of the body is very convenient, and at the same time tolerably accurate.

The aboral disk arises, as already known, as a thickened patch of the ectoderm on the right side of the body, and extends also some distance on to the dorsal side; but as metamorphosis progresses, it shifts its position, so that it becomes more and more inclined to the sagittal plane, and at the same time more nearly parallel to the crossplane, i. e. a plane perpendicular to the chief axis of the body. The position of the dorsal pore remains nearly, although not quite, constant.

From the above it follows that the oral side of the adult is the anterior, the aboral the posterior, the madreporic (interradius) the dorsal, and the side opposite this the ventral, side of the larva. Right and left sides are evident from what precedes.

(2) As has been partly suggested in the foregoing lines, both the definitive mouth and anus are new formations.

(3) Of the body cavity in the larva I distinguish, with Bury, four portions, an anterior and a posterior on either side of the body. In the fully developed Bipinnaria, these portions are all directly or indirectly continuous with one another; but in the course of the Brachiolaria stage the right posterior portion is entirely cut off from the remaining parts, and later, when the tentacles of the Bipinnaria have been largely drawn in, another septum is formed anterior to the first, while the left posterior portion also becomes constricted off from the rest; so that at this stage there are three separate cavities, viz. (1) the right posterior, (2) the left posterior and the right middle portions, which still form but one cavity, and (3) the right and left anterior portions, which freely communicate with each other in the Brachiolaria arms. The anterior cavity (3) persists in the adult as the axial sinus and the water-vascular system.

The right posterior cavity shifts its position hand in hand with the aboral disk, and finally occupies the posterior end of the larva just beneath the disk. With the development of the arms of the star, it sends out diverticula into them, and thus assumes the bibrachiate, 5-radiate star-shape which it has in the adult.

(4) The formation of the water-vascular ring is not a mechanical result of the breaking through of the adult mouth, for the ring exists as such some time before the mouth is formed.

(5) With Bury and MacBride I distinguish sharply two structures, the pore-canal and the stone-canal. There is a stage when the pore-

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canal alone is present. I believe that they are also phylogenetically distinct, the stone-canal being a later formation. In comparing the Echinoderms with such a group as the Enteropneusta it is, as it seems to me, the pore-canal alone that is primarily to be taken into consideration.

(6) The opening of the pore-canal and the stone-canal into the body cavity persists throughout life. This is true not only of *Asterina gibbosa* and *Asterias pallida*, but also of *Asterias tenera*, *Solaster endeca*, and *Cribrella sanguinolenta*, and inferentially of all starfishes. The opening of the stone-canal is always on the right side of the sagittal plane.

(7) In agreement with MacBride, I find that the "dorsal organ" of Bury, the "Centralblutgeflecht" of Ludwig, forms the periœsophageal portion of the body cavity of the adult. It arises in the form of a tube from the left posterior enterocœl just behind the pore-canal. In a young Brachiolaria it encircles about one fourth of the whole circumference of the cardiac portion of the stomach, and it forms a complete ring in a young star that has just finished its metamorphosis. The septum that divides it from the left posterior enterocœl is subsequently completely absorbed except in one place, viz. the madreporic interradius, where it appears to persist throughout the life of the animal. The term "oral cœlom," used by MacBride, seems to me unfortunate, as that term has been applied to another and entirely different cavity (left cœlom) in Crinoids. I therefore prefer to call the structure in question "periœsophageal enterocœl."

(8) The perihæmal spaces (the inner ring excepted) as well as the peribranchial spaces are, according to my observation, of true schizocœl origin.

CAMBRIDGE, April 8, 1896.

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XVIII.

ON THE GROUP OF REAL LINEAR TRANSFORMATIONS WHOSE INVARIANT IS AN ALTERNATE BILINEAR FORM.

By Henry Taber.

Presented February 12, 1896.

Let G denote the group of linear automorphic transformations of the alternate bilinear form

$$\mathfrak{F} = \sum_{1}^{2n}{}_{r} \sum_{1}^{2n}{}_{s} (c_{rs} - c_{sr})\, x_r y_s$$

with cogredient variables and of non-zero determinant. On page 575 *et seq.*, Volume XLVI. of the *Mathematische Annalen*, I have shown that a transformation of group G can be generated by the repetition of an infinitesimal transformation of group G if, and only if, it is the second power of a transformation of group G. I now find, if $\mathfrak{F}$ is real, that the same theorem holds for the sub-group of real transformations of group G. That is, if $\mathfrak{F}$ is real, a real transformation of group G can be generated by the repetition of a real infinitesimal transformation of group G if, and only if, it is the second power of a real transformation of this group. Furthermore, if $\mathfrak{F}$ is real, the second power of a real transformation of group G is the $(2\,m)$th power of a real transformation of this group for any even exponent $2\,m$.*

If the transformation T is defined by the system of equations

$$x'_r = a_{r1}\,x_1 + a_{r2}\,x_2 + \ldots + a_{r,\,2n}\,x_{2n}\ (r = 1, 2, \ldots \overline{2n-1}, 2n),$$

let T_λ denote the transformation defined by the equations

$$x'_r = (a_{r1}\,x_1 + a_{r2}\,x_2 + \ldots + a_{r,\,2n}\,x_{2n}) - \lambda\,x_r\ (r = 1, 2, \ldots \overline{2n-1}, 2n),$$

λ being a root of multiplicity m of the characteristic equation of T.

* For an odd exponent $2\,m+1$, any real transformation of group G is the $(2\,m+1)$th power of a real transformation of this group.

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The nullity * of T_λ is then at least one, and the nullity of successive powers of T_λ increases until a power of exponent $\mu \leqq m$ is attained whose nullity is equal to m. The nullity of the $(\mu+1)$th and higher powers of T_λ is then also m. If we designate respectively by

$$m_1, m_2, \ldots . m_{\mu-1}, m_\mu = m,$$

the nullities of

$$T_\lambda,\ T_\lambda^2, \ldots . T_\lambda^{\mu-1},\ T_\lambda^\mu,$$

then

$$m_1 \geqq m_2 - m_1 \geqq \ldots . \geqq m_\mu - m_{\mu-1} \geqq 1.$$

The numbers μ_1, μ_2, etc., may be termed the numbers *belonging* to the root λ of the characteristic equation of T.

If now T is the second power of a real transformation of group G. the numbers belonging to each negative root of the characteristic equation of T are all even. These conditions are probably not only necessary but sufficient in order that a real transformation T of group G may be the second power of a real transformation of this group.

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* The *nullity* of the transformation defined by the system of equations

$$x'_r = a_{r1}x_1 + a_{r2}x_2 + \ldots + a_{r,N}x_N \quad r = (1, 2, \ldots N),$$

is m if all the $(m-1)$th minors (the minor determinants of order $N-m+1$) are zero, but not all the mth minors (the minor determinants of order $N-m$) of the matrix.

$$\begin{matrix} a_{11}, a_{12}, \ldots \\ a_{21}, a_{22}, \ldots \\ \ldots\ldots \end{matrix}$$

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PROCEEDINGS.

Eight hundred and seventy-fifth Meeting.

May 8, 1895. — ANNUAL MEETING.

VICE-PRESIDENT B. A. GOULD in the chair.

The chair announced the death of James Dwight Dana and John Newton, Associate Fellows.

The Corresponding Secretary read the following letters: from Sir F. Pollock, acknowledging his election as Foreign Honorary Member; and from the Natural History Society of Bonn, announcing the death of its Curator, Reinhard Peck.

The Corresponding Secretary read the Report of the Council.

The Report of the Treasurer was read and accepted. The following is an abstract.

GENERAL FUND.

Receipts.

Balance, May 1st, 1894			$2,301.55
Sale of rights, Mass. Cotton Mills			30.50
			2,332.05
Assessments	$975.00		
Sale of publications	48.52		
Subscriptions for publications	461.00	$1,484.52	
Investments		3,847.50	
Return of bank tax		51.40	
Gift of E. C. Clarke		600.00	5,983.42
			$8,315.47

Expenditures.

General expenses		$2,630.26	
Publishing expenses		1,788.29	
Library expenses		1,221.68	$5,640.23
Balance			2,675.24
			$8,315.47

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RUMFORD FUND.

Receipts.

Balance May 1st, 1894		$4,110.21
Investments	$1786.00	
Return of bank tax	97.55	1,883.55
		$5,993.76

Expenditures.

Books and binding	$120.06	
Rent	10.00	$130.06
Balance		5,863.70
		$5,993.76

WARREN FUND.

Receipts.

Balance, May 1st, 1894	$334.89
Income	840.00
	$1,174.89

Expenditures.

Investigations	$800.00
Balance	374.89
	$1,174.89

BUILDING FUND.

Receipts.

Balance, May 1st, 1894	$418.68
Income	425.00
	843.68
Balance	843.68
	$843.68

On the motion of William R. Livermore, it was

Voted, That the thanks of the Academy be tendered to the Treasurer for his timely gift of six hundred dollars for clerical assistance.

The Librarian made a verbal report on the condition of the library, by which it appeared that 2,773 books and pamphlets were added to the library during the past year, of which 1,866 were obtained by gift and exchange, 645 purchased with the appropriation from the General Fund, and 262 with the appropriation from the Rumford Fund. 465 volumes were

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bound at an expense of $580.15, $35.80 of this amount being charged to the Rumford Fund. The total expenses for books, periodicals, and binding amounted to $1,326.68. There were 242 books borrowed from the library by 32 persons, of whom 23 were Fellows of the Academy.

The following reports were presented: —

Report of the Rumford Committee.

The Academy voted at the annual meeting, May, 1894, to appropriate the sum of one thousand dollars from the Rumford Fund to be expended at the discretion of the Rumford Committee in aid of investigations in Light and heat, payments from this sum to be made on the order of the chairman of the Committee. The Committee has made the following appropriations from this sum: —

$250 to Professor Nichols of Cornell University for investigations in the radiations from carbon at different temperatures.

$250 to Professor E. H. Hall of Harvard University, in aid of his investigations on the thermal conductivity of metals.

$250 to Professor Webster of Clark University, in aid of an investigation upon the relation between the velocity of light waves and electrical waves.

The Committee has also voted to approve the purchase of such volumes of the Memoirs of the International Bureau of Weights and Measures as are needed to complete the set in the library of the Academy, and has also passed the following votes: —

Voted, To recommend to the Academy to appropriate $250 to Professor B. O. Peirce in further aid of his investigation on the thermal conductivities of poor conductors.

Voted, To recommend to the Academy to appropriate $2,000 to the Rumford Committee to be expended at the discretion of the Committee in aid of investigations in Light and heat, payments from this sum to be made on the order of the chairman of the Committee.

Voted, For the second time to recommend to the Academy that the Rumford Medals be awarded to Thomas A. Edison, for his investigations in electric lighting.

JOHN TROWBRIDGE, *Chairman.*

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Report of the C. M. Warren Committee.

8 May, 1895.

In behalf of the C. M. Warren Committee, I have to report that during the past year a grant of six hundred dollars ($600) has been made to Professor C. F. Mabery, of Cleveland, Ohio, in aid of his investigation of American and Canadian Petroleums, and a grant of two hundred dollars ($200) to Professor F. C. Phillips, of Allegheny, Pa., in furtherance of his researches on Natural Gas.

F. H. STORER, *Chairman.*

A report of the Committee of Finance was read and accepted.

On the recommendation of the Committee of Finance, it was

Voted, To appropriate nineteen hundred dollars ($1,900) for general expenses.

Voted, That an appropriation of thirteen hundred dollars ($1,300) be made to the Librarian, and that this appropriation cover also the petty expenses of the Assistant Librarian.

Voted, That an appropriation of eighteen hundred dollars ($1800) be made for Volume XXX. of the *Proceedings*, now in press, provided that a part of this sum be expended for plates.

Voted, That an appropriation of four hundred dollars ($400) be made to be used in the preparation of the plates and printing the text of Roland Thaxter's Memoir on the Laboulbeniaceæ.

On the recommendation of the Rumford Committee, it was

Voted, To appropriate the sum of two hundred and fifty dollars ($250) from the income of the Rumford Fund to B. O. Peirce, in further aid of his investigation on the thermal conductivities of poor conductors.

Voted, To appropriate from the income of the Rumford Fund the sum of two thousand dollars ($2,000), to be expended at the discretion of the Rumford Committee in aid of investigations in Light and Heat, payments from this sum to be made on the order of the chairman of the Committee.

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Voted, To award the Rumford Premium to Thomas Alva Edison for his investigations in electric lighting.

On the recommendation of the C. M. Warren Committee, it was

Voted, To appropriate six hundred dollars ($600) from the income of the C. M. Warren Fund to C. F. Mabery, of Cleveland, Ohio, to aid him in continuing his researches on the chemistry of petroleum.

On the motion of the Treasurer, it was

Voted, That the assessment for the ensuing year be five dollars ($5).

On the recommendation of the Committee on amending the statutes, it was

Voted, To amend chapter 10, section 2, line 8, of the statutes, by changing the word "eight" to "seven."

The following gentlemen were elected members of the Academy: —

Arthur Gordon Webster, of Worcester, to be a Resident Fellow in Class I., Section 2 (Physics).

Arthur Michael, of Boston, to be a Resident Fellow in Class I., Section 3 (Chemistry).

John Fiske, of Cambridge, to be a Resident Fellow in Class III., Section 3 (Political Economy and History).

William Price Craighill, of Baltimore, to be an Associate Fellow in Class I., Section 4 (Technology and Engineering), in place of the late William Helmsley Emory.

The annual election resulted in the choice of the following officers: —

ALEXANDER AGASSIZ, *President.*
BENJAMIN A. GOULD, *Vice-President for Class I.*
GEORGE L. GOODALE, *Vice-President for Class II.*
AUGUSTUS LOWELL, *Vice-President for Class III.*
CHARLES L. JACKSON, *Corresponding Secretary.*
WILLIAM WATSON, *Recording Secretary.*
ELIOT C. CLARKE, *Treasurer.*
HENRY W. HAYNES, *Librarian.*

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Councillors.

BENJAMIN O. PEIRCE,
HENRY MITCHELL,
LEONARD P. KINNICUTT, } of Class I.

BENJAMIN L. ROBINSON,
HENRY W. WILLIAMS,
HENRY P. BOWDITCH, } of Class II.

ANDREW M. DAVIS,
THOMAS W. HIGGINSON,
JAMES B. THAYER, } of Class III.

Member of Committee of Finance.

AUGUSTUS LOWELL.

Rumford Committee.

JOHN TROWBRIDGE, EDWARD C. PICKERING,
ERASMUS D. LEAVITT, CHARLES R. CROSS,
BENJAMIN O. PEIRCE, AMOS E. DOLBEAR,
BENJAMIN A. GOULD.

C. M. Warren Committee.

FRANCIS H. STORER, HENRY B. HILL,
CHARLES L. JACKSON, LEONARD P. KINNICUTT,
SAMUEL CABOT, ARTHUR M. COMEY,
ROBERT H. RICHARDS.

The chair appointed the following Standing Committees:—

Committee of Publication.

CHARLES L. JACKSON, WILLIAM G. FARLOW,
WILLIAM W. GOODWIN.

Committee on the Library.

SAMUEL H. SCUDDER, AMOS E. DOLBEAR,
G. STANLEY HALL.

Auditing Committee.

HENRY G. DENNY, JOHN C. ROPES.

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Henry W. Williams read an obituary notice of Hermann von Helmholtz.

The following papers were presented by title: —

On the Thermal Conductivities of certain poor Conductors. By B. O. Peirce and R. W. Willson.

On the Simultaneous Partial Differential Equations:

$$\frac{(D\,y\,\xi)^2 - a^2\,(D\,x\,\xi)^2}{D\,y\,\xi} = f(\xi);$$

$$a^2\,D^2\,x\,\xi - D^2\,y\,\xi = 0.$$

By B. O. Peirce.

On certain Derivatives of unsymmetrical Tribrombenzol. By C. L. Jackson and F. B. Gallivan.

Trinitrophenylmalonic Ester. By C. L. Jackson and J. I. Phinney.

On Phenoquinone. By C. L. Jackson and G. Oenslager.

On the Nitrite of Bromdinitrophenylmalonic Ester. By C. L. Jackson and J. H. Moore.

On Dinitrobromtoluol and some of its Derivatives. By C. L. Jackson and M. H. Ittner.

Contributions from the Gray Herbarium of Harvard University, New Series, No. 9: — 1. On the Flora of the Galapagos Islands, as shown by the Collections of Dr. G. Baur. 2. New and noteworthy Plants, chiefly from Oaxaca, collected by C. G. Pringle, L. C. Smith, and E. W. Nelson. 3. A Synoptic Revision of the Genus *Lamourouxia*. By B. L. Robinson and J. L. Greenman.

Studies in Morphogenesis. 3. A Preliminary Catalogue of the Processes concerned in Ontogeny. By C. B. Davenport.

On the motion of the Recording Secretary, it was

Voted, That it is expedient to publish in the *Memoirs* Roland Thaxter's paper on Laboulbeniaceæ.

Eight hundred and seventy-sixth Meeting.

October 9, 1895. — STATED MEETING.

The PRESIDENT in the chair.

The chair announced the death of Edward Samuel Ritchie, Harold Whiting, and Henry Willard Williams, Resident Fel-

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lows; Daniel Cady Eaton, William Wetmore Story, Associate Fellows; and Thomas Henry Huxley, Louis Pasteur, Sven Ludwig Lovén, and Carl Friedrich Wilhelm Ludwig, Foreign Honorary Members.

The Corresponding Secretary presented the following letters: from the International Catalogue Committee of the Royal Society of London; from the Royal Society of New South Wales, announcing the conditions of competition for its medal; from the Royal Academy of Sciences of Turin, announcing the death of its Secretary, Giuseppe Basso; from the family of Etienne Léopold Trouvelot, announcing his death; and from the Physico-economical Society of Königsberg, announcing the death of its Honorary President, Franz Ernst Neumann.

The following gentlemen were elected members of the Academy: —

Paul Sebastian Yendell, of Dorchester, to be a Resident Fellow in Class I., Section 1 (Mathematics and Astronomy).

Hammond Vinton Hayes, of Cambridge, to be a Resident Fellow in Class I., Section 2 (Physics).

Benjamin Kendall Emerson, of Amherst, to be a Resident Fellow in Class II., Section 1 (Geology, Mineralogy, and Physics of the Globe).

Marie Alfred Cornu, of Paris, to be a Foreign Honorary Member in Class I., Section 2 (Physics), in place of the late Hermann Ludwig Ferdinand von Helmholtz.

Jacobus Henricus van't Hoff, of Amsterdam, to be a Foreign Honorary Member in Class I., Section 3 (Chemistry), in place of the late Jean Charles Galissard de Marignac.

John Trowbridge exhibited and read extracts from a collection of letters written by Count Rumford to Marc Auguste Pictet, and presented to the Academy by Jules Marcou, who obtained them from the late Auguste de la Rive. It was thereupon

Voted, That the thanks of the Academy be tendered to Jules Marcou for his valuable gift.

Voted, That the letters be referred to the Rumford Committee and the Committee of Publication.

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Eight hundred and seventy-seventh Meeting.

November 13, 1895.

The CORRESPONDING SECRETARY in the chair.

The chair announced the death of Asahel Clark Kendrick, an Associate Fellow.

A letter was read from Thomas W. Higginson, tendering his resignation as Councillor.

The following papers were presented by title: —

Thermo-electric Interpolation Formulæ. By Silas W. Holman.

Melting Points of Aluminum, Silver, Gold, Copper, and Platinum. By S. W. Holman, with R. R. Lawrence and L. Barr.

Pyrometry: Calibration of the Le Chatelier Thermo-electric Pyrometer. By Silas W. Holman.

Calorimetry: Methods of Cooling Correction. By Silas W. Holman.

On some Points in the Development of Æcidia. By Herbert M. Richards.

William E. Story gave an informal talk on the new methods of representing mathematical surfaces, and exhibited Plateau's apparatus and a variety of models.

Eight hundred and seventy-eighth Meeting.

December 11, 1895.

The Academy met at the house of the President, at Cambridge.

The PRESIDENT in the chair.

The resignation of Thomas W. Higginson as Councillor was accepted.

The following papers were read: —

On the Temperature of the Crust of the Earth at great Depths. By Alexander Agassiz and P. C. F. West.

Palestine in the Fifteenth Century B. C., according to recent Discoveries. By Crawford H. Toy.

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Eight hundred and seventy-ninth Meeting.

January 8, 1896. — STATED MEETING.

The PRESIDENT in the chair.

The Corresponding Secretary read letters from A. Cornu and J. H. van't Hoff, acknowledging their election as Foreign Honorary Members; and one from B. K. Emerson, accepting Fellowship.

The vacancies in the Council occasioned by the death of Henry W. Williams and the resignation of Thomas W. Higginson were filled by the election of

WILLIAM M. DAVIS, of Class II.,
HORACE E. SCUDDER, of Class III.

The following gentlemen were elected members of the Academy:—

Augustus St. Gaudens, of New York, to be an Associate Fellow in Class III., Section 4 (Literature and the Fine Arts), in place of the late William Wetmore Story.

Hermann Graf zu Solms-Laubach, of Strasburg, to be a Foreign Honorary Member in Class II., Section 2 (Botany), in place of the late Marquis de Saporta.

Carl Gegenbaur, of Heidelberg, to be a Foreign Honorary Member in Class II., Section 3 (Zoölogy and Physiology), in place of the late Thomas Henry Huxley.

Willy Kühne, of Heidelberg, to be a Foreign Honorary Member in Class II., Section 4 (Medicine and Surgery), in place of the late Charles Edouard Brown-Séquard.

The President alluded to the fact that the Massachusetts Historical Society had informally signified to the Academy its willingness to make a ten years' lease of quarters in its proposed building on the Back Bay. After a brief discussion, it was

Voted, That the question of securing new quarters for the Academy be referred to the Committee of Finance, to report at the next meeting.

On the motion of the Corresponding Secretary, it was

Voted, To meet, on adjournment, on the second Wednesday in February.

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Edwin H. Hall presented by title a paper On the Thermal Conductivity of Mild Steel.

Henry Taber announced that he had proved the sufficiency of certain conditions that in Volume XLVI., page 583, of the *Mathematische Annalen*, he had shown to be necessary in order that a transformation of the group whose invariant is a certain linear complex may be generated by the repetition of an infinitesimal transformation of the group.

Eight hundred and eightieth Meeting.

February 12, 1896. — ADJOURNED STATED MEETING.

The PRESIDENT in the chair.

The chair announced the death of Martin Brimmer and Richard Manning Hodges, Resident Fellows.

The Corresponding Secretary read a letter from Augustus St. Gaudens, acknowledging his election as Associate Fellow.

The President reported that no change of quarters for the Academy was feasible at present.

George L. Goodale read a paper on Forestry under New England Conditions.

John Trowbridge gave an informal account of his experiments with the cathode rays.

No evidence of refraction was detected. Wooden lenses, both double convex and double concave, were tried, and apparently did not affect the rays. In Helmholtz's discussion of the electro-magnetic theory of light, there is a longitudinal wave which travels with an infinite velocity. Such a wave, travelling faster than the velocity of light, would not suffer refraction. The photographs procured by the new rays are not strictly shadow pictures, such as may have been obtained before in the electro-static field. They show a specific absorption which is a new phenomenon. For instance, a disk of microscopic cover glass, $\frac{1}{100}$ of an inch thick, perfectly transparent to the ordinary rays of light, throws as strong a shadow as a board one inch thick. The bones of the hand throw a stronger shadow than the flesh surrounding them.

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The new phenomenon promises to be of great assistance in studying the extremities of the human body, and in detecting the presence of metallic bodies and fragments of glass in them. A shot, placed on the back of the hand, can be photographed through the flesh of the thickest portion of the hand. Of course, therefore, it could be detected if it were imbedded in the hand.

Pictures have been taken at the Jefferson Physical Laboratory, after an exposure of one minute, which show the bones of the hand, and there is no doubt that the time of exposure can be reduced to a few seconds for certain portions of the extremities. The Crookes tubes can be protected from injury by immersing their terminals in a suitable oil, — preferably, boiled linseed oil.

The following paper was read by title: —

On the Group of real Linear Transformations whose Invariant is an Alternate Bilinear Form. By Henry Taber.

Eight hundred and eighty-first Meeting.

March 11, 1896. — STATED MEETING.

VICE-PRESIDENT B. A. GOULD in the chair.

The Corresponding Secretary read letters from Carl Gegenbaur, W. Kühne, and H. Graf zu Solms-Laubach, acknowledging their election as Foreign Honorary Members; from the Natural History Society of Bonn, announcing the death of its Secretary, Philipp Bertkau; from the Joint Commission of the Scientific Societies of Washington, D. C., with regard to the proposition for a Director in Chief of Scientific Bureaus in the Department of Agriculture.

On the motion of the Corresponding Secretary, it was

Voted, To meet on adjournment on the 8th of April.

W. M. Davis read a paper on the Outline of Cape Cod.

C. L. Jackson made the following announcement: —

C. L. Jackson and A. M. Comey have found that potassic cobalticyanide is converted by boiling nitric acid into a red jelly, having the formula $KH_2Co_3(CN)_{11}H_2O$, from which a silver salt, $Ag_3Co_3(CN)_{11}H_2O$, and a barium salt, $BaHCo_3(CN)_{11}1\frac{1}{2}H_2O$,

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were obtained. All of these substances have been analyzed. Potassic ferricyanide gives a similar black jelly under the same conditions.

On the motion of Eliot C. Clarke, the following resolutions were adopted: —

Whereas, The Committee on Coinage, Weights, and Measures of the National House of Representatives has reported a bill requiring the early adoption of the Metric System of Weights and Measures by all Departments of the Government, and its adoption by the whole nation, at a subsequent fixed date, as the only legal system, —

Resolved, That the American Academy of Arts and Sciences, renewing its recommendation made in former years, urges Congress to consider favorably this bill, and thus permit the United States to join the majority of civilized nations as regards its system of weights and measures.

Resolved, That this Academy believes that the universal adoption of this system will aid researches in physical science, and also commercial transactions, and will tend to bring about the fraternity of nations.

Resolved, That copies of these resolutions be sent to the presiding officers of the two Houses of Congress, to the Senators from Massachusetts, to the chairman of the Committee of Finance of the Senate, and to the chairman of the Committee on Coinage, Weights, and Measures of the House.

Eight hundred and eighty-second Meeting.

April 8, 1896. — ADJOURNED STATED MEETING.

The Academy met at the Walker Building of the Massachusetts Institute of Technology, Boston.

VICE-PRESIDENT B. A. GOULD in the chair.

The following gentlemen were elected members of the Academy: —

John Stone Stone, of Boston, to be a Resident Fellow in Class I., Section 2 (Physics).

Robert Wheeler Willson, of Cambridge, to be a Resident Fellow in Class I., Section 2.

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Theobald Smith, of Boston, to be a Resident Fellow in Class II., Section 4 (Medicine and Surgery).

Charles Lane Poor, of Baltimore, to be an Associate Fellow in Class I., Section 1 (Mathematics and Astronomy), in place of the late James Edward Oliver.

Robert Simpson Woodward, of New York, to be an Associate Fellow in Class I., Section 4 (Technology and Engineering), in place of the late John Newton.

Basil Lanneau Gildersleeve, of Baltimore, to be an Associate Fellow in Class III, Section 2 (Philology and Archæology), in place of the late William Dwight Whitney.

Thomas Raynesford Lounsbury, of New Haven, to be an Associate Fellow in Class III., Section 2, in place of the late Asahel Clark Kendrick.

Karl Theodor Weierstrass, of Berlin, to be a Foreign Honorary Memberr in Class I., Section 1 (Mathematics and Astronomy), in place of the late Arthur Cayley.

Michael Foster, of Cambridge, Eng., to be a Foreign Honorary Member in Class II., Section 3 (Zoölogy and Physiology), in place of the late Carl Friedrich Wilhelm Ludwig.

Alexander Onufrijevič Kovalevskij, of St. Petersburg, to be a Foreign Honorary Member in Class II., Section 3, in place of the late Sven Ludwig Lovén.

Karl Weinhold, of Berlin, to be a Foreign Honorary Member in Class III., Section 2 (Philology and Archæology), in place of the late Sir Henry Creswicke Rawlinson, Bart.

Friedrich Hermann Grimm, of Berlin, to be a Foreign Honorary Member in Class III., Section 3 (Philosophy and Jurisprudence), in place of the late Sir John Robert Seeley.

On the motion of the chairman of the Rumford Committee, it was

Voted, To present the Rumford Medal by proxy at the annual meeting.

David G. Lyon gave an informal talk on recent Assyrian discoveries, with illustrations.

E. L. Mark presented the following paper by title: —

Preliminary Notes on the Embryology of the Starfish (*Asterias pallida*). By Seitaro Goto.

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AMERICAN ACADEMY OF ARTS AND SCIENCES.

REPORT OF THE COUNCIL. — PRESENTED MAY 13, 1896.

BIOGRAPHICAL NOTICES.

RICHARD MANNING HODGES	BY DAVID W. CHEEVER.
HAROLD WHITING	JOHN TROWBRIDGE.
EDWARD SAMUEL RITCHIE	AMOS E. DOLBEAR.
MARTIN BRIMMER	WILLIAM EVERETT.
HENRY WHEATLAND	F. W. PUTNAM.
JAMES EDWARD OLIVER	GUSTAVUS HAY.
VISCOUNT FERDINAND DE LESSEPS	HENRY MITCHELL.

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REPORT OF THE COUNCIL.

Since the annual meeting of the 8th of May, 1895, the Academy has lost by death thirteen members: — five Fellows, Martin Brimmer, Richard Manning Hodges, Edward Samuel Ritchie, Harold Whiting, and Henry Willard Williams; four Associate Fellows, Daniel Cady Eaton, Atticus Greene Haygood, Asahel Clark Kendrick, and William Wetmore Story; four Foreign Honorary Members, Thomas Henry Huxley, Sven Ludwig Lovén, Carl Friedrich Wilhelm Ludwig, and Louis Pasteur.

RESIDENT FELLOWS.

RICHARD MANNING HODGES.

Dr. Richard Manning Hodges was born in Bridgewater, Massachusetts, November 6, 1827. He was fitted for Harvard College at the Boston Latin School, and was graduated in 1847.

Dr. Hodges took the degree of A. M. in due course, and that of M.D. in 1850. He was Demonstrator of Anatomy from 1853 until 1861. In 1866 he was appointed Adjunct Professor of Surgery. He resigned his professorship in 1872.

In 1863 he was chosen one of the visiting surgeons of the Massachusetts General Hospital. In 1885 he resigned his position, and gave up the practice of surgery. In 1891 he entirely ceased to practise.

His last illness was short, and he died on February 9, 1896.

Dr. Hodges served twice on the Board of Overseers of Harvard College. He was a Resident Fellow of the American Academy of Arts and Sciences.

As a man he was sincere, straightforward, open, just, positive, punctual, not to say punctilious. Possessed of a strong body, he was

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active, and an untiring worker. He held the confidence of his patients to a remarkable degree. He was a good diagnostician; a logical reasoner; and possessed great common sense.

He was equally loyal to his profession, and to his brother physicians. As an anatomist he was exact and thorough; expert and dexterous, his dissections were more than excellent, they were beautiful.

He contributed largely and wisely to the Warren Anatomical Museum with the work of his own hands. Many of his preparations of coarse anatomy are, and will remain, unsurpassed.

From practical anatomy to surgery the step was short. He became a rapid and skilful operator. He was also so well grounded in Surgical Pathology that he was a thoughtful, level-headed, and much valued consultant.

As a writer he was concise and clear. His "Dissector" went through several editions, and was of the utmost value to students. Unsullied by pictures, it lightened the work of the young anatomist by clear and true descriptions, by accuracy, and by brevity. His essay on the "Excision of Joints" won the Boylston Prize in 1861.

His observations on "Spiroidal Fractures" and on "Pilo-nidal Sinus" were original. His latest work was a "History of the Discovery of Anæsthesia," which will endure as a complete and careful account of that great surgical event.

Dr. Hodges did a large share of public gratuitous service in the Cholera Hospital; in the Boston Dispensary; at the Massachusetts General Hospital; at the State House during the Civil War, on the examining board for surgeons; and also as a volunteer surgeon sent to the seat of war.

His quick and buoyant manner, his keen insight, decision of character, and honesty, would have insured success in any pursuit; and they won for him an enduring reputation as a skilled anatomist, a bold yet conservative surgeon, and a reliable observer and physician.

1896. DAVID W. CHEEVER.

HAROLD WHITING.

PROFESSOR HAROLD WHITING was born in Roxbury, May 13, 1855. He was fitted for Harvard University at the Roxbury Latin School, and graduated from the University with the degree of A. B. in 1877, of A. M. in 1878, and of Ph. D. in 1884. He was Instructor in Physics in the University from 1883 to 1891. In 1892 he was appointed Associate Professor of Physics in the University of Cali-

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fornia, and was lost at sea, with his wife and four children, while returning to Cambridge, on May 27, 1895.

This bare recital of the principal epochs in his life is like a mere pen and ink sketch of a vivid personality, lacking color, and conveying no adequate idea of the man whose career was so suddenly closed. This personality was so intense that one feels it difficult to realize that he has left us, and one half expects to meet him on turning some corner.

He early manifested a remarkable aptitude for scientific subjects. When little older than six or seven, it is related that he used to sit in an arm-chair for long periods, his head sunk on his breast, and when spoken to he would say, "Please don't interrupt me! I have almost got the theory." He was always observing, as well as thinking, even before he could speak plainly, coming home from drives or walks with such revelations as this: "I have found that an island is a steady thing."

My attention was first called to Whiting when he was a Sophomore. I was hearing a recitation in Physics, and had made some remarks upon a scientific point. He arose and stoutly denied the truth of my assertion. The class tried to suppress him by hissing, and by "Wooding up," but he maintained his ground. I found that he was right, and from that time began to observe him more closely. He was both morally and physically courageous. While sailing in the harbor of Plymouth he was capsized, and remained for a long time in a perilous position in the water shut in by a fog. At length a fisherman hove in sight. Whiting, immersed in the water, took off his hat and made the fisherman a low bow. The latter remarked, "Had n't you better git in?"

Dr. Whiting had a keen sense of humor mingled with a subtle wit. There was nothing unkind in this wit, for he had too generous a heart to knowingly wound any one. On looking over the proof of one of his scientific papers I was puzzled by a certain involved mathematical expression, and turned to him for an explanation. It was in reality a very simple formula, and he remarked, in apologizing for its abstruse form, "I have been so much annoyed by the involved mathematical expressions of the English school of mathematicians that I determined to give them a nut to crack."

Dr. Whiting's idiosyncrasies were so strong that no team work was possible for him. He could not be hitched up with any one. His mind seemed to play about a subject much as certain forms of electricity dart hither and thither about a summer cloud, frequently illumining

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obscure regions in a surprising way. It was highly interesting to see him make an imperfect piece of apparatus give wonderfully good results; and while he was Instructor in Physics in the Jefferson Physical Laboratory he was of great service to the department, acting like a skirmisher in the growing subject of Laboratory teaching of Physics. Those who followed him profited both by his mistakes and his successes, and could afford to pardon the mistakes, which were those of a courageous explorer in a new field. His fertility of mind was remarkable, and he often said of himself that he was like a codfish which lays a million eggs, and only one or two perchance hatches. This fertility and brilliancy were such that many of those with whom he was associated often remarked that they would not be surprised if Whiting should hit upon something remarkable in Science. If he had discovered, for instance, the X-rays, many of us would have said, "It was just like Whiting to look through his hand at a Crookes tube."

The physical department of Harvard University is indebted to him for many valuable suggestions, and also for pecuniary contributions. He did not hesitate to aid it whenever he saw its needs, and by his will he gave twenty thousand dollars for Fellowships in Physics in Harvard University.

His scientific work began with an investigation of magnetic waves on iron and steel rods, which was published in the Proceedings of the American Academy of Arts and Sciences. His thesis for the degree of Doctor of Philosophy in Harvard University was on the Theory of Cohesion. While Instructor in the University he published a Syllabus of a Hundred Physical Measurements, for the use of the Jefferson Physical Laboratory; and also a valuable treatise on Physical Measurements, consisting of three large volumes. While at the University of California he also published full sets of laboratory notes. When we examine his life's work we find that it gave a decided stimulus to the modern laboratory method of teaching Physics by quantitative experiments rather than by qualitative. If he had elaborated many of his ingenious methods into papers for periodicals, the list of his works would have been much longer.

Many could come forward and testify to his generous hand, as well as to his generous mind. With his rich qualities of scientific imagination, experimental skill, and mathematical ability, joined to the steadiness of middle age, much could have been expected of him. He still lives in his gift to the young Physicists of the University.

1896. JOHN TROWBRIDGE.

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EDWARD SAMUEL RITCHIE.

EDWARD SAMUEL RITCHIE, son of John and Eliza (Eliot) Ritchie, was born in Dorchester, Massachusetts, August 18, 1814. After living some years in Dorchester, his father moved to North Bridgewater. During the years 1827 and 1828 he attended school at the Friends Academy in New Bedford. In 1829 he was taught by Rev. John Goldsbury, in North Bridgewater, studying mornings and working for a furniture maker in the afternoons, as he had mechanical aptitudes, and wished to learn the use of tools.

Early in life he showed great interest in art and in science. He was the only surviving child of a family of six, and his father gave him every advantage to help him in studies in which he was particularly interested. His health was extremely delicate in youth, and that added to a very sensitive nature prevented him from taking a collegiate education, which his father was anxious he should have. He had a laboratory to work out experimentally what interested him, and was a very close student. Having great power of concentration, he was entirely oblivious to everything around him when he was particularly interested in any subject.

He had also a great love for music, and was a good musician, giving his services as an organist for several years to the Episcopal Church in New Bedford, in which he was senior warden.

While living in New Bedford he constructed a telescope for his own use, which he afterwards sold to the Friends Academy, where he had formerly been a scholar.

He was much interested in sculpture, and has left very creditable work in several cameos and a nude figure, two thirds life-size, of a nymph of his own posing. He made the clay figure, plaster cast, and cutting in marble, doing all the work from the beginning. He thought seriously of going to Rome to make that art a life study, but, being a devoted son, was unwilling to be separated from his aged mother.

In 1850 he entered into partnership with N. B. Chamberlain, a philosophical instrument maker. His business previous to this had never been pleasant to him, but this was quite to his taste. After a short time the partnership was dissolved, and Mr. Ritchie continued the business alone.

His improvement in the induction coil brought him into public notice. In 1851 Ruhmkorff of Paris constructed the coil which yet bears his name. He succeeded in producing sparks about two inches in length. Ritchie perceived that the defect of the Ruhmkorff coil was insufficient

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insulation of the secondary coil. He concluded that, if this were divided into sections properly insulated from each other, the device would be more efficient and give a longer spark. On trial, his expectations were realized. One of these coils was exhibited at a meeting of the British Association held in Dublin in 1857, and afterwards at the University of Edinburgh. A description of Ritchie's coil was published in Silliman's Journal and in the Journal of the Franklin Institute. M. Ruhmkorff procured one, and, copying it successfully, received a prize from the French government for it, — a proceeding which greatly disappointed Mr. Ritchie, who was entitled to it. The improvement of Mr. Ritchie transformed the coil from being a toy giving a two-inch spark to an instrument capable of giving a flash two feet or more in length, and approaching the characteristics of lightning.

At the time of our Civil War Mr. Ritchie's attention was called to the need of a better compass for our navy. The English Admiralty Compass, considered the finest in the world, was in general use at that time. In order to aid his study in making his improvements in this instrument, he made a support so constructed as to give the motions of a vessel at sea.

After much thought and labor he invented the Monitor and Liquid Compasses. The former did good service during the war, and the latter was at once adopted by the Navy, and is now in use all over the world.

He also constructed about that time another instrument which was a great help to the Navy, the Theodolite, fastened to a pendulum hanging in a tank of water, which enabled surveys to be taken of the harbors on the Atlantic and Gulf coasts. For these inventions of high merit he will be long remembered by the scientific world.

He was an exceedingly conscientious man, and was ever ready to help others over difficulties which he had overcome himself, and sometimes such persons received the credit and financial profit which rightly belonged to him.

He died on June 1, 1895, in his eighty-first year.

1896. A. E. Dolbear.

MARTIN BRIMMER.

The various distinguished bodies to which our deceased associate, Hon. Martin Brimmer, belonged, have already paid him such varied and appreciative tributes that a detailed biography, in the ordinary sense of the word, would be quite out of place. Nor was his life itself so distinguished by striking adventures or significant dis-

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coveries that a biographer could find the details, if he were disposed to use them. As far as his life had a story, it is shortly told.

Martin Brimmer was the son of Hon. Martin and Harriet [Wadsworth] Brimmer, and was born in Boston, 9 December, 1829. His father was a well known and most public spirited citizen, twice Mayor of Boston. For him is named the Brimmer School, and on the older maps of Boston T Wharf is described as "Brimmer's T." Our associate entered the Sophomore Class of Harvard College at the age of sixteen, and graduated in 1849. Without being distinguished as a scholar, he won the very peculiar regard of all who were associated with him, as instructors or companions, even under circumstances where many young men would have made a different impression. He travelled in Europe soon after graduation, and soon after his return began a connection with a great number of literary and charitable societies as trustee, with one or other of which he was constantly engaged to the last. He was chosen a Fellow of Harvard College at an unusually early age, but with universal approval, and, having resigned this post, was again chosen to it and held it till his death, sitting for a part of the interval on the Board of Overseers. He was a member of the Massachusetts House of Representatives in 1859, 1860, and 1861, and of the State Senate in 1865. He was a Presidential Elector in 1876, and a candidate for Congress in 1878. In 1869 he was chosen the first president of the Boston Museum of Fine Arts, and held the post till his death. He visited Europe and Egypt more than once after his first journey; and in the early days of the struggle for the territory of Kansas, had travelled there to find out for himself the truth of a situation so passionately discussed by opposing partisans. A journey in Kansas in 1855 was a more arduous affair than one to Egypt a generation later. Mr. Brimmer died January 14, 1896. This may be said to be his biography, unless one gave a detailed list of all the bodies of which he was the devoted, energetic, intelligent servant, — unless, also, one went into the details of private life, where Mr. Brimmer indeed shone with an unequalled light, but one whose lustre was far too tender and sacred for public exposure.

But if life means not events but character, not what one has done but what one has been, Mr. Brimmer's is a memory which it is peculiarly incumbent on us to record and to cherish. In Virgil's matchless and immortal roll of those who have won eternal happiness, he ranks with the patriot soldier, the inspired bard, the stainless priest, and the keen inventor, "those who have made others remember

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them by deserving it." No man ever deserved to be remembered better than our late associate.

He was born and brought up in the midst of all those things which are commonly held to excuse and incapacitate men from hard work. He had an ample fortune, so secured that it might be enjoyed and not dissipated; he had an assured social position, which exempted him from all toil or strife to bring his name into prominence; and a slight physical infirmity might have been held in his case, as in that of the historian Prescott, rather to justify idleness than otherwise. Mr. Brimmer yielded to none of these allurements. He conceived that he held all his personal and social advantages as in trust for the community. He positively enjoyed to work for the strengthening of all that is good, and the suppression of all that is evil, in modern society. By example and by precept, by personal labor and by contributions of money, perhaps most of all by the fact that he was known to be always upon the side of what was high, noble, strong, and lovely, whether he was actually speaking, giving, or working, he was a living proof that what are sometimes censured or ridiculed as the showy fungi of a decaying civilization may be really the healthy flowers of a new and hopeful republic.

The thoughtful student of our society, its merits and its wants, must see clearly that one serious danger to our happiness and prosperity arises from the temper of second thought, — of suspicion and distrust of ourselves and others. A vast number of our ablest, wisest, and most virtuous citizens seem unable to execute their highest purposes without tormenting themselves all the time by some speculation as to what secondary effect their action may have on themselves or others. Mr. Brimmer combined with the soundest and most cultivated intelligence an absolute simplicity of character. Open or reserved as the case demanded, whenever he did speak or act he was perfectly sincere. He was by no means without honorable ambition; but it was an ambition held in strict subservience to courtesy, to honor, and to conscience. He was firm in his opinions and distinct in their expression; but it could only be a very mean or a very brutal person who could be offended by his high-minded and polite refusal to agree to what he thought wrong. The word "culture," so sadly soiled and travestied at the present day, had in Mr. Brimmer its perfect fulfilment. He stood to uncultivated men as an apple does to a crab. In this age, which fancies mere tartness or bitterness constitute flavor, such a presence as his was a living instance of how much the raciest nature is improved by the development of sweetness and tenderness.

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Of all Mr. Brimmer's public services, if we are to make the invidious task of selection, the highest place may be given to his work in the Art Museum. Perhaps other men could have filled his place in other institutions equally well; in this he was without a possible rival. By disposition and training alike, he was fitted to be a perfect judge and patron of fine art; and if Boston is ever to keep her head above the overwhelming gulf of pretension and mediocrity that is pouring over the country in matters of art, she will owe her salvation to him more than to any single man. This work elicited from him other work of exquisite power, for which his adaptation had hardly been suspected. He delivered one or two addresses on the importance of the fine arts, which were not merely sound, elegant, and manly, but rose in more than one passage to thrilling and convincing eloquence of a kind rare indeed in these days.

This Academy, like the community, was the better for his membership, and his place will long be unsupplied.

1896 WILLIAM EVERETT.

HENRY WHEATLAND.

HENRY WHEATLAND was elected a Fellow of the Academy in 1845. He was born in Salem, January 11, 1812, and died there, February 27, 1893. His father was Richard Wheatland, born in Wareham, Dorset County, England, in 1762, who came to America in 1783. For several years he sailed from the port of Salem as commander of vessels in the India trade. In 1801 he retired from the sea and became one of the prosperous India merchants who helped to make the fame of the old town in the palmy days of its commerce. In 1796 Captain Wheatland was married to his second wife; and Henry was the sixth and youngest child of this marriage. As a boy he was of a delicate constitution, and, being naturally disposed to study, his parents had him fitted for college in the Salem schools. At the age of sixteen he entered Harvard, and was graduated in the class of 1832. His taste for natural history was evidently formed in boyhood, for we find that in the last year of his college course he was active in the formation of "The Harvard Linnean," of which college society he was the Secretary. The Constitution of this society, as he wrote it, is among his papers. This was probably the immediate precursor of the present Harvard Natural History Society, which was formed in 1837. On leaving college he returned to Salem and became an active worker in the Essex County Natural History Society and the Essex Historical Society.

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In order to carry on his scientific studies he followed the course which seemed at that time almost essential to a student of natural history; he entered the Harvard Medical School, attending lectures in Boston in the winter and studying with Dr. Abel L. Pierson in Salem during the remainder of the year. In 1837 he received the degree of M. D. That it was not his intention to practise medicine, unless forced by circumstances to earn a living in that way, I know from frequent conversations with him and from his advice to me, when, aroused by Agassiz' visit to Salem, in 1856, I wished to accept the offer made to me to become his student. At that time Dr. Wheatland said, "You can go to Cambridge and study under Agassiz, Wyman, and Gray, and prepare yourself to enter the Medical School and become a doctor, as I did; then you can get your living in that way, if you have to, and study natural history too. That is the way most naturalists have done." In my early days, and still more in his, to follow natural history as a profession and a means of livelihood was hardly to be considered. It is evident that Dr. Wheatland gave as much attention to the comparative anatomy of animals as he did to the special anatomy of man, for during this time he prepared many skulls and skeletons for the collection of the Essex County Natural History Society, which, with others prepared at a later time, are still preserved in the Peabody Academy of Science in Salem.

The Doctor was always filled with a quiet enthusiasm for his work, never demonstrative, and even painfully reserved in his manner in public; only those who knew him best and were by their work closely associated with him found out his true nature, and realized how much he accomplished in his quiet, persistent way. Many a time I have seen the face of this reserved and quiet man beam with delight on obtaining some skull new to the collection, or when bringing up in his little dredge a seaweed or shell new to him. Often when in a dory dredging off the shore of Winter Island, Marblehead, Swampscott, or Manchester, his favorite localities for a half-day's outing, I have seen him as enthusiastic and happy over the contents of the little dredge as any naturalist of to-day could be on seeing for the first time the animals brought up from great depths by the modern appliances. I think it can be safely claimed for Dr. Wheatland, that he was the first to dredge in our New England waters, and I believe he was the first naturalist in America to adopt this means of collecting animals and plants living on the ocean bottom at moderate depths.

It was during the most active time of his natural history days that the Geological, Botanical, and Zoölogical Survey of the State was car-

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ried on, and the Doctor contributed his full share in specimens and observations during his constant association with Emerson, Storer, Gould, Harris, and others; while Stimpson of a later date always acknowledged that he took his first lessons in dredging of Dr. Wheatland. To Agassiz he sent many specimens when the latter began to make his famous Museum at Cambridge; and with many conchologists abroad he carried on active exchanges, which added much to the early importance of the natural history collections in Salem. For years after I became intimately associated with him, in my boyhood, in the work of the Essex Institute, the Doctor continued his preparation of skulls of such mammals as he could obtain, many heads being brought home to him from foreign countries by Salem sea captains. These heads the Doctor soaked in tubs of water kept in the yard at his home, and bleached on shelves he prepared for the purpose on the roof of the barn. He daily watched and worked over these specimens for hours at a time, and finally placed them clean and white in the cases in the Institute. In those days every collector was obliged to prepare his own specimens; and if a rare fish or reptile came to the Society and there was no money for the purchase of alcohol, which was generally the case, the Doctor would prepare the skin and "mount" the specimen. It was his hands that prepared, over sixty years ago, the large specimen of horse-mackerel which still hangs upon the walls of the Peabody Academy of Science, and the enormous lobster, the wonder of the present day, which is treasured by the Academy.

It was the Doctor's practice of saving in some way every important specimen which he secured that made the series of "stuffed" turtles and their prepared shells and skeletons of such importance as to call Agassiz to Salem. On this occasion I was first brought in contact with the great naturalist, which event changed the whole course of my life; and it was thus through the training of Doctor Wheatland that I entered upon my career of scientific pursuits. In acknowledging him, my life-long friend, as my first instructor in science, I but give credit due to one who helped many others in a similar manner, — one whose friendship was always true and lasting, and whose usefulness and influence in the community were widespread.

While Dr. Wheatland was a true naturalist and did much to encourage the study in others, and unquestionably aided to a considerable extent the impetus given to its study in Salem, he became in later years equally interested in local historical and genealogical researches. As younger men gradually took up his natural history work, he turned his attention wholly to historical matters and his brain became a

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wonderful treasure-house of genealogy and local history. While he published but little, he was ever helping others to prepare papers. Many were the hours and days he gave to rendering such assistance, and to making critical revisions of manuscripts submitted to him. It was in such work that his kindly nature was tested to the utmost, but never did he refuse to give to others for use or publication the results that he had worked long and diligently to secure. I have often heard him remark, "It makes no difference who publishes or gets credit for a fact that I have found, so long as it is made known to the world, or a mistake is corrected."

The life work of such a man as Henry Wheatland would naturally culminate in some important result to the community in which he lived, and the result of his life work can be best expressed by the words *The Essex Institute.* This important and remarkable institution is his memorial. Henry Wheatland is rightfully the acknowledged founder of the Essex Institute. It was through his efforts that in 1848 two societies were brought together which for a number of years had their home and principal membership in Salem, — the Essex Historical Society and the Essex Institute. To the subjects already fostered by these societies was added the encouragement of art and horticulture. The formation of a library was also included in the new organization, and plans were made for the publication of the Proceedings of the Institute and of scientific and historical papers.

Of this Institute Dr. Wheatland was the Secretary and sustaining power, giving of his moderate competence to its needs, and working day and night for its advancement, without compensation or thought of reward except in the successful growth of the institution and the acknowledgment of its usefulness by the community. From the small beginnings of nearly half a century ago, the Institute has grown as a sturdy tree of knowledge. It now has a considerable membership of devoted workers, who appreciate what has come to them and realize its usefulness and influence in the community. It has a home of its own and considerable invested property, which insure its perpetuity. It is a power for education and culture, and for all that calls forth the higher aspirations of man. It has set an example which has been followed in many places, and it has added to the sum of human knowledge by its numerous publications. Such has been the result of the life and labors of Henry Wheatland, – that gentle persistent worker whose aim was ever to help others in their researches; to save from destruction for the use of the future student the manuscripts he would require in his studies; to furnish to the people the ready means of obtaining a knowl-

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edge of the natnral history of the region by forming a perfect collection of the rocks, minerals, plants, and animals of Essex County; to practically encourage the cultivation of fruits, flowers, and vegetables; to form a scientific and historical library for the benefit of all who wished to study; to foster research and to aid in the diffusion of knowledge. All this Doctor Wheatland lived to see carried forward far beyond his expectations. He died content with his work; and he has left a priceless legacy to the city of his birth. With his death the last of the old school of naturalists has passed away. New methods and new theories have made rapid advances, and a second generation, after his active working days, has entered the ever-widening field of scientific research, until now the times are changed, and instead of its being necessary to become a doctor of medicine in order to be a naturalist, a physician must be something of a naturalist in order to hold his position in the medical profession.

1896. F. W. PUTNAM.*

ASSOCIATE FELLOWS.

JAMES EDWARD OLIVER.

JAMES EDWARD OLIVER, who died on March 27, 1895, in the sixty-sixth year of his age, was born in Portland, Maine, July 27, 1829, of Quaker parentage. The family subsequently removed to Lynn, Massachusetts, and there young Oliver fitted for college at the Lynn Academy. He entered Harvard as a Sophomore, graduated in 1849, and was the class poet.

One of his classmates writes of him that "he was a modest, diffident, retiring, self-absorbed person in college, doing work not to be ashamed of in other branches, but achieving distinction only in mathematics."

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* In these brief reminiscences of the career of Dr. Wheatland, and of the remarkable influence he exerted on the life of many young men and women, as well as upon the community in which he lived, I have not attempted a sketch of his life, nor have I alluded to many events of special interest. Some of these, and a list of the important offices he held, the societies that conferred membership upon him, and the titles of his publications, are to be found in the pamphlet published by the Essex Institute, containing an account of the meeting of the Essex Institute held on April 17, 1893, "in memory of its late President"; also in the Memoir by William P. Upham, printed in the Proceedings of the Massachusetts Historical Society, 1895; and in memorials of various other societies.

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It may be added that he was one of the ablest pupils of the elder Peirce.

With regard to his mathematical ability, Cajori * writes that "in 1849 he had already displayed extraordinary mathematical power," and "in the Harvard Catalogues of 1854 and 1855 we find J. E. Oliver taking advanced courses of mathematics such as were offered at that time by no other institution in the land."

Shortly after graduation he received an appointment in the Nautical Almanac office in Cambridge under Professor Peirce, where he met several men of unusual mathematical ability.

In 1861 he was elected a Fellow of this Academy, and in 1873 an Associate Fellow. In 1871 he was appointed an Assistant Professor of Mathematics at Cornell University, and in 1873 he was appointed Professor, and retained the office during his life.

He was also a Fellow of the American Philosophical Society, of the American Association for the Advancement of Science, and of the National Academy. He was also a member of the Council of the American Mathematical Society.

Professor Oliver's published communications on mathematical subjects may seem fewer than might have been expected, considering his great ability. He seems to have been actuated less by a regard for reputation than by what he considered as his immediate duty. Mrs. Oliver writes that "his chief original work was done before his advanced students," and that, "when his intellectual curiosity was satisfied, he begrudged the time necessary to write it out for publication."

Professor Burr (Cornell Daily Sun, April 3, 1895) writes of him that "his mind was too discursive in its method and too unpractical in its bent to lead him largely into publication, and it is as a teacher and a man that he will be longest and most affectionately remembered. He was absent-minded, unmethodical, prone to digression, but his acuteness of mind, his power of sustained research, his comprehensiveness of view, his utter freedom from bias, his unflagging enthusiasm, made his leadership for those who had the wit and mettle to follow it a thing of perpetual inspiration."

Besides these peculiarities of his intellectual temperament, if I may use such an expression, which were without doubt unfavorable to publication of original results, there was also another difficulty. The excessive work required of him as mathematical professor at Cornell

* Bureau of Education, Circular of Information No. 3, 1890, p. 178. The Teaching and History of Mathematics in the United States, by Florian Cajori, M. S. (University of Wisconsin), etc. Washington, 1890.

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left him little time for the preparation of his material for publication. He has alluded to this in one of his official reports.

In the Appendix to the Annual Report of the President of Cornell University for 1886–87, Professor Oliver (see Cajori, *loc. cit.*) writes: "We are not unmindful of the fact that by publishing more we could help to strengthen the university, and that we ought to do so, if it were possible. Indeed, every one of us five is now preparing work for publication, or expects to be doing so this summer, but such work progresses very slowly, because the more immediate duties of each day leave us so little of that freshness without which good theoretical work cannot be done. . . . The greatest hindrance to the success of the department, especially in the higher kinds of work, lies, as we think, in the excessive amount of teaching required of each teacher, — commonly from seventeen to twenty or more hours per week."

I am indebted to Mrs. Oliver for the following list of Professor Oliver's published notes and papers connected with mathematics.

Demonstration of the Pythagorean Proposition. Math. Monthly, Vol. I., 1858, p. 10.

On Mr. Collins's Property of Circulates. Math. Monthly, Vol. I., 1859, p. 345.

Introduction to Treatise on Determinants. Math. Monthly, Vol. III., 1860, p. 86.

Partial Investigation on the best approximate Representation of all the Mutual Ratios of k Quantities by those of Simple Integers. Proceedings of American Academy of Arts and Sciences, Vol. VI.

Mathematical Note on Linguistic Resemblances. Trans. Amer. Philos. Soc., Vol. XIII.

On some Focal Properties of Quadrics. Proceedings American Academy, Vol. VII.

Note on Query concerning Ball held in Jet of Water. Analyst, I. 29, 1874.

On the Law of Distribution for certain Plant-Numbers. A Method of finding the Law of Linear Elasticity in a Metal. Abstract Proceedings Amer. Assoc. Adv. Sc., Vol. XXXI. 1882.

A Projective Relation among Infinitesimal Elements. Annals of Math., Vol. I., May, 1884.

On the General Linear Differential Equation. Annals of Math., Vol. III., August, 1887.

Elementary Notes. I. General and Logico-math. Notation. Annals of Math., Vol. IV., December, 1888.

Preliminary Paper on Sun's Rotation. Read before the Spring Meeting of the National Academy, 1888.

The Soaring of Birds. Science, January 4, 1889.

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Some Difficulties in Lasage-Thomson Gravitation Theory. Abstract Proceedings Amer. Assoc. Adv. Sc., Vol. XLI., 1892.

A Mathematical Review of the Free-will Question. Phil. Review, Vol. I., March, 1892.

Review of Mathematical Recreations, by W. W. Rouse Ball. Bulletin N. Y. Math. Soc., November 1, 1892.

Estimates of Distance. Science, March 11, 1892.

Oliver, Wait, and Jones. Text-books on Mathematics for Colleges. Algebra, especially chapter on Imaginaries, etc. Trigonometry.

Cornell University. Reports on Courses, Aims, and Methods of Mathematical Teaching at Cornell University.

Papers and Discussions at various Educational Meetings on Teaching, with application to the study and teaching of Mathematics.

The above sketch refers to matters which, being related to his scientific career, present themselves more easily to our notice.

But this was only a part of his life. Professor Oliver was interested in much outside of his special duties as teacher of mathematics. His moral qualities were of a superior order. His personal relations with his friends and colleagues were such as to gain for him their respect and affection.

But I feel that any attempt on my part to portray the social and moral side of his life would be inadequate, and must refer for information in this regard to the affectionate notices* of him written by those who had enjoyed the privilege of intimate companionship with him, and who regarded him as a man of exceptionally exalted character.

1895. G. HAY.

FOREIGN HONORARY MEMBERS.

VISCOUNT FERDINAND DE LESSEPS.

IN the biographical notice that follows we do not expect to make an adequate exhibit of the work and honors of a life so long and impetuous as that of M. de Lesseps, but hope, by presenting the salient points in his career, to indicate what manner of man he was, from first to last, without intruding mere opinion.

Of his boyhood we know very little, except that he had every advantage of refined social life and education. As he reached manhood he found himself down at the front where volunteers for the

* See Christian Register, May 2, 1895; Cornell Daily Sun, April 3, 1895; The New Unity, Chicago, August 1, 1895.

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advance were called, and he went forward. Fortune was inconstant, but he never looked back. For more than a half century he was the most conspicuous and interesting figure in the rush of the busy world; — he turned its tide, but it overtook him and whelmed over him when his footsteps faltered in old age. He was the hero of one generation, and the victim of another.

He was born at Versailles in the year 1805, and educated at the Lycée Napoléon for the foreign service, to which the family had a sort of traditional claim. His grandfather, Martin de Lesseps, was Consul at St. Petersburg before the Revolution, and his father, Matthew de Lesseps, held the Commissariat-Generalship of Egypt at the time that Ferdinand was born. Subsequently he was Imperial Commissary at the Seven Islands (Ionian), where he won the good will of everybody, and in the fantastic diction of the period he was declared to be "liberal even to fanatical generosity." In 1817 he was sent on a mission to Morocco, and shortly after appears as French Consul at Philadelphia, where he assisted at a Commercial Convention, and was elected a member of the American Philosophical Society. He married Mademoiselle de Grivegnir, daughter of a distinguished jurist in Malaga. It was through this Spanish mother that Ferdinand de Lesseps came to be a kinsman of the Empress of the French, in the unfolding plot of this family's missions.

The first professional employment for Ferdinand was offered by his uncle, Jean Baptiste de Lesseps (best known to scientific men as that Viscount de Lesseps who, in 1787, crossed Siberia from the Okhotsk Sea to bring a report — which proved to be the last tidings — from La Pérouse). This uncle in 1825 was French Consul at Lisbon, and Ferdinand, then twenty years old, was sent by him on a diplomatic errand. Shortly after this we find him a "student consul" at Alexandria, under his father, Matthew de Lesseps.

In 1833 he was given a sub-consulate at Cairo. It was in the following year that the great plague broke out, memorable as perhaps the most fatal visitation of modern times. Young Lesseps was then left in management of the Consul-Generalship, and he won such golden opinion that he was decorated with the cross of the Legion of Honor. In 1838 he went as Consul to Rotterdam, in 1839 to Malaga. It was as French Consul at Barcelona that he won, during the revolt of 1842, the admiration of Europe as a humanitarian. His personal courage and his devotion to suffering people induced four governments to send him decorations. He was made an officer of the Legion of Honor. The city of Marseilles awarded him a medal, and the city of Barcelona

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caused his bust to be set up. A few years later he received the insignia of Chevalier of the Grand Cross of Isabella the Catholic.

In 1848 he was summoned to Paris by Lamartine, and sent as Minister Plenipotentiary to Madrid. After about one year he was withdrawn by Prince Napoleon, and sent in the same capacity to Rome, at the time of Garibaldi's occupation, — "a man," said M. Odilon Barrot, "who enjoys our full confidence, whom we have put to the test in very trying circumstances, and who has always served the cause of liberty and humanity."

M. de Lesseps has told the vexations of his Roman mission very interestingly in his "Recollections," but with singular absence of personal consciousness even in failure. He often defends himself, and designs to do so; but it is always an argument for the merit of the work upon which he is engaged, rather than any declaration of his own higher motives, except that he attributed all his successes to the energy of "patriotism," — a word which seemed to embrace about all the world. He seems to have used this word simply as the most modest admissible expression for public duty, and the obligation to serve in the great march.

He learned in the foreign service to respect and sympathize with earnest people everywhere, and formed enthusiastic friendships among even those of radically different blood and radically different traditions. To bring people together in some common interest and intent seemed to him to be the cure for national prejudice, and he saw in foreign trade this catholicon. In the administration of foreign affairs during periods mostly peaceful, he acquired a pretty clear impression of those larger principles of reciprocal trade that escape the merchant's more short-sighted view. The consulates were for him not only schools of commercial jurisprudence, but they enabled him to distinguish the interest of the community from that of the individual. An obstruction or difficulty in the path of trade may be of value to the few who know or can afford the roundabout way; but it is the mission of public spirit to equalize opportunities as well as to shorten process. M. de Lesseps, in his letter to Cobden (1854), advised those statesmen who opposed the Suez Canal because it would reduce the number of ships and men by shortening the route to India, to induce shipmasters to take the Cape Horn route, and thus employ more men and more ships. This retort is a pretty good illustration of his way of meeting disingenuous criticism by the *reductio ad absurdum*.

In this earlier part of his life, following in the footprints of his fathers, he often missed complete success, — although always in

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earnest. But all the while he was unwittingly fitting himself for his true mission, and gaining strength, and knowledge, and courage for a practical interpretation of a sublime thought: "*Je veux détruire cette muraille de sable qui arrête le progrès.*"

This *muraille de sable*, this wall of sand, separates two worlds. In one, man plays the roll assigned to him in the original setting of the piece; in the other, he assists in never-ending creation. In one he awaits his orders in harness, in the other he is charioteer. But from whichever point of view we look backwards across the Isthmus, from Islam or from Christendom, history foreshadows the canal. And now that it is finished and in full operation, so that its direct effects upon the commerce of the world have ultimated, one reads the history of trade by a new light, which discovers prophetic meaning in many events that anticipated this new dispensation.

If we seek the origin of the idea, we are taken back to a remote past; and we may follow the thought down through a hundred generations, which it dimly pervades, till the sifting of the French Revolution discovers its "fixity, that true sign of the law"; thenceforth, it is a pressing obligation hastening to maturity.

In Napoleon's message to the Directory, "Whatever European power holds Egypt permanently is in the end mistress of India," he put the cart before the horse, as we have since learned; but the necessity for the canal in the scheme of human progress is reflected even in such inverted conceptions, and to the short-lived Egyptian Institute we owe the first scientific investigation of the problem of joining the two seas, although the errors of survey, which deferred the project by placing the two seas out of level, reflect little credit upon the pupils of the Normal School. To make errors that should prove stepping stones to the truth was, however, in the spirit of the age; and the report of Lapère — reasserting "the *wisdom of the ancients*," that had already afflicted and separated the nations of the earth for thirty-five hundred years — only aroused a new and defiant generation, that with better observations and in better temper reconciled the two seas forever.

M. Mimut, "one of the most distinguished diplomats ever in the service of France," holding the great work of the French expedition in his hands, gave to M. de Lesseps the first quickening thought, and from that moment his mind and heart received the ancient hope renewed, and he became its champion. It was a religious experience. "You have," said Renan, addressing him at the Academy, "caused to blossom once more a flower which seemed faded forever. You

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have given to this sceptical age of ours a striking proof of the efficacy of faith."

We are satisfied that here is the point of view from which the confidence and the enthusiasm of M. de Lesseps is comprehensible. How could he possibly have expected to convert such a man as Lord Palmerston? The result of their interview was that M. de Lesseps doubted the sanity of the Premier, while the latter regarded him as an adventurer, — a soldier of fortune, — employed, perhaps, in the interest of some French "move" in Egypt. In reality, there stood before the great statesman a simple-minded Da Gama, who had discovered a new route to India and offered himself as the pilot. It was nobody's interest then to make him a figure-head, — he was at the other end of the ship; it was his trick at the wheel.

After the failure of the Egyptian expedition, Napoleon, in 1803, instructed Matthew de Lesseps, Political Agent in Egypt, to nominate for election and for the Sultan's approval an officer of ability to serve as Pasha of Cairo. M. de Lesseps named one who was then in command of a regiment of Basha Bazouks, a Macedonian, who could neither read nor write, and who had come to Egypt as a subordinate of contingents. This man was Mehemet Ali, — the wise and terrible, — who subsequently made himself master and mortgagee of Egypt. It was he who built the Mahmoudieh Canal, — the last, and perhaps the greatest, of non-militant works ever executed by unaided human hands. He also inaugurated work on the Barage — the dream of Hassan — over which Egypt had brooded five hundred years; and it was he that discovered the potential energies of young Lesseps, whom he caused to sit at his feet and listen to the narrative of his slaughter of the Mamelukes, and the now possible project of a cut through to Suez, which the Viceroy was ready to undertake, under a grand *corvée*, except that he feared the would-be and could-be mistresses of India.

It was at this time (while consular pupil in 1832) that Ferdinand de Lesseps became the companion, and incidentally the teacher, of Saïd Pasha, the son of the Viceroy, on whom was laid the futurition of the father's dream, — and the dream of all the Pharaohs. The "memorandum" prepared for this prince by M. de Lesseps, long after, connects itself in our minds with these boyhood days, when he says, "The names of the Egyptian sovereigns who erected the Pyramids remain unknown, — the name of the prince who opens the great maritime canal will be blessed from century to century down to the most distant posterity," — so well did this "grand Frenchman" understand and share the hope of glory upon which he counted.

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Ever since the establishment of British power in India, the best minds in England had seen the necessity of securing a right of way across the Delta of the Nile, and a step in this direction seemed to be made in the treaty of Warren Hastings in 1776; but nothing came of it till the vigorous movement of Mehemet Ali to open a transit route via the Mahmoudieh Canal brought Waghorn to the front in 1829, — the Indian mail service really opened two years later, — although it was not till 1840 that a steamship company used the Red Sea route. Young M. de Lesseps was witness of Waghorn's triumph, and, more than all the world besides, did him the honor of a just appreciation. He was an example and an inspiration all his life, and when his own hour of triumph arrived he raised a statue to Waghorn at Suez.

Professional detractors discover, now, that the Suez Canal never really presented any physical difficulties or dangers; but how many of this class resisted the heresies of the French expedition, or forsook them at the bidding of a Bourdelau? Many of us are old enough to remember when in popular belief the two seas were out of level, the sand storms of the desert buried caravans and armies, and thousands of dead fellaheen were used each month to raise the banks of the Mahmoudieh Canal. Children in our Sabbath schools were taught these things of the land of Mehemet Ali, — that bold bad Napoleon of Islam. And yet the *Revue des Deux Mondes*, away back in 1835, ventured to say, "Mehemet Ali is working for Europe, which will become his heir."

None of these bugbears troubled the mind of M. de Lesseps, who was the first to declare that the Isthmus was only a *muraille de sable qui arrête le progrès*. This was not the "bluff" of the speculator, but the faith that moves mountains. Yet, as late as July, 1852, in a letter to the Consul General of Holland in Egypt, he says, "I confess that my scheme is still in the clouds, and I do not conceal from myself that, as long as I am the only person who believes it to be possible, that is tantamount to saying it is impossible." At this time he had forsaken Egypt and was setting up a model farm in the Berry district and restoring the castle of Agnes Sorel. Abbas Pasha was then Viceroy of Egypt, and this prince knew not Joseph. It was under this Viceroy that the English Transit Railway was built.

In 1854, when M. de Lesseps was nearly fifty years old, Abbas Pasha died, and the "sympathetic Mohammed Saïd" became Viceroy of Egypt, and immediately sent for his old master to return; and before the close of the year, the concession of powers for the formation of the canal company had been issued.

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A few little touches of nature in the journal of Lesseps, at this critical turning point of his career, reveal the entire consecration of every faculty to the great mission of his life. As he left his tent in the early morning of that anxious day, when the Viceroy was to hear his story and decide upon building the canal, he beheld a rainbow in the sky: "I confess that my heart beat violently, and that I was obliged to put a rein upon my imagination, which was tempted to see, in this sign of alliance spoken of in the Scriptures, the presage of the union between the Western and the Eastern world, and the dawning of the day for the success of my project." And again, on the same day, "When I leave the Viceroy to go and get my breakfast, I jump my horse over the parapet. You will see that this foolhardy act was one of the reasons that induced the Viceroy's *entourage* to support my scheme, — the generals at breakfast telling me as much." On the same day there was target practice, and a whole regiment had failed to hit the mark. M. de Lesseps seized a musket and put a bullet through the bull's-eye. Again, as he stood there, a bird hovered in the sky, — he raised his piece and fired, — an eagle fell at his feet. Even misfortune betokened success, as when on the Nile his cabin took fire and he was severely burned, he said, "The accident was of good omen, in that we had acquitted our debt to ill luck." Later, he found himself accidentally a lodger in the building which had once held the Institute of Egypt, and "this too was a good sign." All signs point our way when we are on the right road.

The gods were propitious, the prince was gracious. M. de Lesseps did not pause to consider whether these gods were of his own creation, or this prince only his docile pupil. Besides, he was not alone to carry the burden of this project, even in its initial stage. He had taken two friends into his counsels long ago. These were Linant Bey and Mougel Bey, engineers of the Barage and countrymen of his. These three put their earnings together, and with a capital of six thousand dollars they formed the nucleus of the "Compagnie Universelle."

Linant Bey had long before tried to raise a company to build the canal, and he and Bourdelau had run double lines of levels reconciling the two seas. He had also traced a line of location, which was very nearly that adopted in exploitation. Mougel, well known since as the chief engineer of the Barage, was recognized as the essential third point of support. In his journal of this initiatory period, M. de Lesseps notes down his dependence upon the knowledge, skill, and devotion of these two friends; and in his days of greatest glory he published

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these notes, that all the world might be just to those who ventured with him in the forlorn hope.

These three kindred spirits, with only the Bible for their guide-book, made a reconnaissance of this route. The journal of Lesseps, which contains over twenty quotations from the Old Testament, is full of the confidence and courage of hope and health. In that desert land the skies are clear and the north wind full of joyous life and stored up energies. The whole horizon is in view, and he who has singleness of purpose may march straight to his destiny, whether he holds the Koran or the Bible. And here we are minded of that fearful contrast offered by the Isthmus of Panama on the other side of the earth, — with its weary mountains and dark forests breaking down the trade winds, and shortening and degrading the vision till high hopes and purposes are starved out, and man becomes a timid, sickly animal.

We agree that, as it turned out, the Suez Canal did not involve the solution of any new problems of physics, or very greatly tax the skill of French engineers. Indeed, it was not the practical and direct difficulties that really made the nations timid. In "this wall of sand," separating the Moslem from the Christian world, there lay sealed up with the seal of Solomon afreet and genii that made nations tremble to think of; for these, rashly let loose, might disturb the balance of power and throw out of adjustment trade and industries all over the world. It proposed radical change, and who could tell what might happen? Engineers and laborers stood ever ready to do the work, but the world waited for the prophet who could forecast a healthy and happy result. M. de Lesseps filled this office. His training, his knowledge, and his enthusiasm commanded respect. His promises of advantage east and west once seemed florid beyond the measure of his careful computations and great array of statistics, but, as we read his articles now, we are struck with his acuteness of foresight and his moderation.

He seems to have been a man of unusual singleness of purpose, — in something wider than a moral sense, — and to have absorbed himself absolutely in the work before him without ulterior design. He was in politics a republican, but he "never even from curiosity attended a political meeting." He was a partisan of the Prince President, but he could not follow him in the *coup d'état*, and only submitted to the Empire in the interest of peace, — and the canal. The Empress was a kinsman of his, and he had rendered her, in her humbler life, a personal service which she requited in personal good will. These relations may have procured for him the *entrée* to the

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family circle, and brought the Emperor within the sphere of good influence. French journals were quick to discover an epigram, — the expression of good omen: "The marriage of two families, and the marriage of two seas." And this ran through the newspapers all around the world: "There is an Arab proverb (much affected by M. de Lesseps) quite apposite here: 'The dogs bark, — the caravan passes.'"

M. de Lesseps was not, by early training, an engineer, but a diplomat. To us his real assimilated rank is that of a discoverer. Why not, as well as Da Gama and Magellan? These declared that a ship could reach the Pacific Ocean by sailing *around* the continents, and they proved it. De Lesseps declared that a ship could reach the Pacific Ocean by sailing *through* the continents, — and he proved it. "He discovers who proves," said Aristotle. None of these men originated a new thought, but each of them did a new thing for the relief of mankind. Vasco de Gama was a prize drawn in a lottery in answer to prayer. He received his instructions through a great prince; and the miracle of his selection and vicarious appointment raised him above all fear. M. de Lesseps presents the antithesis. He was a volunteer who taught princes a good doctrine, and held them down to it. "Hear me for my cause" was all he asked, and those who paused to listen fell under the spell of his enthusiasm and received his testimony.

That was a period of great strain, when Robert Stephenson, one of his own professional caste, turned upon him in Parliament and spoke of his project as "one of those chimeras so often formed to induce English capitalists to part with their money, the end being that these schemes leave them poorer, though they make others much richer." The good temper and even the good sense of M. de Lesseps gave way, and he crossed the Channel to demand explanation. The explanation was made, and we are constrained to say that, if M. de Lesseps had not long afterwards, in his old age, published the correspondence, we should have overrated these contending champions of land and sea.

We can appreciate the causes for anxiety that afflicted intelligent men of affairs in Great Britain. Any change in the course of trade involves national risk. In this way the Venetian Indian trade had dwindled away after the Cape route was opened; then arose Portugal and Holland, to be outdone by England only after a tremendous struggle. Who could say which way the wheel might turn if the Egyptian Transit Railroad came to be supplanted?

England hardly attempted to disguise her apprehensions of danger

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to her trade from the success of the canal built by a rival nation ; but when she prevailed upon the Sultan to order the withdrawal of the fellah labor, our American journals charged her with complacent hypocrisy, and very naturally, since she had just completed the Transit Railway under the corvée in its most cruel form. Under this corvée, Egypt had always draughted men for public works, much in the same way that other countries procure soldiers in time of war. In a country whose existence is involved in a system of canals of irrigation and dikes, there must be no hesitation at critical moments.

M. de Lesseps had prevailed upon Mohammed Saïd greatly to modify the corvée so far as to provide wages and hospitals, but the Viceroy insisted that the abolition of the system would ruin Egypt. Inducing the peasant to work for government by offers of reward was an untried experiment, and one too dangerous to try, since its failure involved, as alternative, the calling in of foreign labor, — an abomination to the Egyptian. England's suggestion that, to avoid the foreign force, the dimensions of the canal should be reduced to the capacity of the native labor, was perfectly logical, and consistent with her alarm policy. But England's policy, like our own, is the net result of conflict among varied interests, theories, and sentiments. The Transit Railway had been practically a national interest, and in the *composition of forces* this interest had been strong enough to determine the direction of the *resultant* till the work was finished. But reports from the scene gradually aroused the humanitarians, who threw their weight into the scale where the interests of the fellahs seemed to lie. In this way, Lord Palmerston, wholly misunderstanding the signs of the times (as events proved), worked more wisely than he knew, and the spell that had darkened Egypt from her birth broke forever.

M. de Lesseps — always single in his purpose — made the withdrawal of the corvée another stepping stone to success. He procured the reference of the question of damages to the Emperor of the French, who made a generous decision in his favor, — far too generous, perhaps, but it enabled the company to introduce machinery in place of hand labor, till the Suez plant excelled that in use in any other part of the world.

The writer of this notice, who made an inspection under full authority from M. de Lesseps the year before the canal was opened, can bear witness that never before or since, in his long experience, has he seen laborers so kindly cared for and so free under the most absolute discipline. M. de Lesseps said, " I have no difficulty in controlling my laborers, because I treat them kindly and make them comprehend

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that they are working for all mankind." His labor then was drawn from many races, but did not include the "sambos," "bravos," coolies, and mongrels of Panama.

His sympathies were always with the fellaheen, even to his own prejudice. He had lived among them, they had served him, and when the struggle came for the possession of the canal he did not ask that it should be French, but that it should be neutral under a pledge from Araby Pasha, the chief of revolting fellaheen and Arab troops. One can hardly conceive of a professional diplomat so blind to his own interests and the interests of the *Compagnie Universelle*, but, like his grandfather of the Seven Islands, "he was generous even to fanaticism."

It must not be overlooked that the Suez Canal is an extension of the Mediterranean and an improvement upon the old route of trade between Europe and Asia, along which ports have been made, warehouses established, and political relations adjusted. Its opening was an easement to all the world. Its construction was sure, because it was the next legitimate step forward under the pressure of an enormous demand. It was, as it proved, no experiment. The ground had been profiled and bored, the climate had been tested and found healthy and cheerful; and laborers were near at hand, not likely to suffer in temper and spirits from the slight change of scene. In short, there were no difficulties, except familiar vicissitudes — and the pride of kings.

The successful opening of the Suez Canal, near the close of 1869, induced throughout the world, perhaps for the first time, a conviction of common interest. The struggle in Egypt had been with the common enemy, and the victory belongs to us all. It was the old allegory adapted to our age, with Count de Lesseps in the part of St. Michael. Among the Mohammedans, as among Christians, there are sects that believe in an internal sense of the word. To these, human life and history, and all events, both great and small, are allegories, and he who catches so much as a glimpse of the esoteric meaning of the piece plays his part like a god. This is the source of enthusiasm.

Some newspaper men are comparing the traffic of the Sault de Ste. Marie with that of the Suez Canal, — as if these two works were of the same world-wide interest, or of the same dramatic import. There may be more tonnage passing through the lock at the "Soo" than through the desert of Suez, and there may be more yet passing through a city street, but the gonfalon was borne by the *Compagnie Universelle*.

During the construction of the canal, we never heard of a single

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American purchaser of a share. Yet these shares are worth now many times their original face value, and we, indirectly or through foreign ships, are among the best customers. The Report for last year shows that of the three thousand three hundred and fifty-two ships that passed through the canal (averaging considerably over two thousand tons each) England sent two thousand three hundred and eighty-six and the United States only five.

Since the days of the Conquistadors, the project for a canal through the American isthmus had been an alternative to the shorter route to the Indies by way of Suez, to be considered in case physical or political difficulties should intervene. The completion of the Suez Canal and the guaranty that British control gave it, reduced very much the commercial demand for the westward route. Nevertheless, the immense revenue at Suez excited the popular mind, especially in France, with the hope of a great speculation in the establishment of a rival company, which, while sharing in some measure the overflowing trade of India and China, might secure the interchanges between the two coasts of America, and perhaps the whole of our trade with Japan.

The Panama project was high born and burst into life a full grown scheme. There were no prime ministers, emperors, and sublime portes lying in wait to stifle it. With Count de Lesseps for its godfather holding the lamp of Aladdin, all the world attended its baptism with complacent expression, — except, perhaps, that the Monroe Doctrine cast a sinister shadow over the scene, — a very thin shadow, but enough to depress the market for the securities after the first rush was over. But what the scheme lacked from first to last was justification in immediate necessity. It had an illegitimate and premature birth, and its sponsors limited their risks to broker's charges, — except M. de Lesseps, who gave all. He gave his past earnings in the best service of our age, and he gave his fair fame as endowment enough for the whole credit of the company — at the start.

Professor Nourse and other clever writers have said that the American canal would be of greater benefit than the Egyptian, because it would connect greater oceans, and that commerce demands a navigable zone around the world. Half in sympathy with these ideas, we cannot help thinking that in this aphoristic form they lack practical merit. Man does not inhabit the sea, and the road that traverses or connects intimately the most inhabited portions of the earth must be the most valuable. Our system of overland railways to the Pacific is practically a supplement to the Suez Canal in the all around commerce of the world, and it was the building of this system with its connec-

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tions that for many years diverted our capital from the ocean, to which it reluctantly returns.

"Fear only the unforeseen" is a classic proverb, much affected by the French, but among no other people has it less practical honor. For the Panama project, the almost unprecedented depth of the cut, the peculiarly obdurate ledges, the great rainfall interrupting labor and causing sloughing of the banks, the necessity for turning the Chagres River, were difficulties weighed and discounted at the start, by able engineers and by a very large and very intelligent company in France. But the "bodily slipping of the hills," in the excavations near the summit level, was a frightful disappointment. It necessitated a postponement of the sea level cut, and the adoption of a scheme of locks, which involved the ponding of the Chagres River. This *change of base* was fatal, and the company broke. A new company has been formed and may keep the project alive till a stronger call from the commercial world comes to its aid.

The King of Spain, looking from his chamber window, shaded his eyes and said, "I am looking for the walls of Panama, — they have cost enough to be seen from here."

With regard to the charges of fraud against the financial management of the Panama Canal Company, we do not feel competent to speak, except to call attention to their diminution as investigations proceed. But with regard to the waste of plant, it does not seem in undue proportion to the magnitude of the experiment. Charges of waste were made against the Suez Canal Company, — especially by our journals and those of other distant people, — and they attend all great enterprises. The plant that does not prove equal to the new work must be cast aside, and lost, if far away from the junk market. The greatest and most successful works that we have visited are strewn with wreckage, marking the field where the battle was won.

Throughout the whole period of the construction in Egypt, M. de Lesseps was actual manager in chief. Many thousands worked under his direction, holding all gradations of rank, but he was the real master spirit. His reports from the beginning are full of acknowledgments of the services and merits of his subordinates. At the outset he leaned upon the superior engineering of Linant Bey and Mougel Bey, and for many years preceding the completion of the canal his reports place Voisin Bey in the foreground, not as a shield from responsibility, but as the support of an enthusiastic company whose millions were thus insured. In his old age, the dependence upon others necessarily became greater and greater, and in the

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Panama scheme he no longer verified the statements of the engineers by adequate inspection and exploitation, but absolutely fell back upon others. His old attitude of control and command continued, but he merely indorsed the reports of the chiefs of divisions, — *whose figures, we now know, were correct,* — without discovering their misleading limitations. His famous promise that the canal should be open to the passage of vessels in 1889 was based, as he stated, upon the unanimous acquiescence of his chiefs of division. Moreover, if we plot on profile paper the amount of work done from date to date, the curve of increments, projected, seems to justify the prediction. His own belief in it is enthusiastically stated in his "Recollections of Forty Years," and he adds: "I am an octogenarian. Old age foresees, and youth acts." This last *mot* was lost upon the public, who saw him now only as the figure-head of a brave ship given over to pirates.

In 1869, the year of the triumphal opening of the Suez Canal, M. de Lesseps was sixty-four years old. This is the age of compulsory retirement for our United States Engineers. But M. de Lesseps was so vigorous that he was for many years later a most valuable man in council. He aided the ship canal of Corinth, and the grand canal from the Elbe to the Baltic. It was not until he was seventy-six that the *Société du Canal de Panama* was constituted, and he was eighty when he crossed the ocean to make a personal inspection of the work in progress. The execution for a year or two, under the full contracts, seemed to realize his predictions, and warrant great expectations; but after that everything went wrong. The master's mind failed before he could have discovered how much he had been betrayed. He lived to be eighty-nine, and died a poor man. His widow and her children are now dependent upon a pension from the Suez Canal Company.

1896. HENRY MITCHELL.

NOTE. — The foregoing had been written out for transmission to the Academy, but was withheld under misgivings as to the adequacy of our very much foreshortened view of the causes of the failure at Panama, until Mr. Nathan Appleton (American Agent of the Panama Canal Company) sent us the last word spoken on the subject by a *competent* witness. This was in the form of a biographical notice by M. Gabriel Gravier, which the Countess de Lesseps sent to Mr. Appleton with her autograph indorsement. This writer takes the ground that all was going well, till a senseless panic upset the market. "The work was marching to a certain success; the original

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estimate had proved very nearly sufficient. Whence came the cyclone which swept away the company and its four hundred thousand shareholders? From Paris, the distracted brain of France!" With some personal and professional knowledge of the American isthmus, and from reading the recent reports of Kimball, Rogers, and others, we distinctly see that the difficulties in the Panama scheme were really intrinsic, — although not insurmountable, — and we have let our account stand.

The Academy has received an accession of ten Resident Fellows, six Associate Fellows, and ten Foreign Honorary Members.

The Roll of the Academy, corrected to date, includes the names of 196 Fellows, 96 Associate Fellows, and 73 Foreign Honorary Members.

May 13, 1896.

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LIST

OF THE

FELLOWS AND FOREIGN HONORARY MEMBERS.

(Corrected to August 1, 1896.)

RESIDENT FELLOWS. — 195.

(Number limited to two hundred.)

CLASS I. — *Mathematical and Physical Sciences.* — 73.

SECTION I. — 18.

Mathematics and Astronomy.

Solon I. Bailey,	Arequipa, Peru.
Seth C. Chandler,	Cambridge.
Alvan G. Clark,	Cambridgeport.
J. Rayner Edmands,	Cambridge.
Benjamin A. Gould,	Cambridge.
Francis M. Green,	Boston.
Gustavus Hay,	Boston.
Henry Mitchell,	Boston.
Edward C. Pickering,	Cambridge.
John Ritchie, Jr.,	Boston.
John D. Runkle,	Brookline.
T. H. Safford,	Williamstown.
Edwin F. Sawyer,	Brighton.
Arthur Searle,	Cambridge.
William E. Story,	Worcester.
Henry Taber,	Worcester.
O. C. Wendell,	Cambridge.
P. S. Yendell,	Dorchester.

SECTION II. — 21.

Physics.

A. Graham Bell,	Washington.
Clarence J. Blake,	Boston.
Francis Blake,	Weston.
John H. Blake,	Boston.
Charles R. Cross,	Boston.
Amos E. Dolbear,	Somerville.
Edwin H. Hall,	Cambridge.
Hammond V. Hayes,	Cambridge.
Silas W. Holman,	Boston.
William L. Hooper,	Somerville.
William W. Jacques,	Newton.
Alonzo S. Kimball,	Worcester.
T. C. Mendenhall,	Worcester.
Benjamin O. Peirce,	Cambridge.
A. Lawrence Rotch,	Boston.
Wallace C. Sabine,	Cambridge.
John S. Stone,	Boston.
Elihu Thomson,	Lynn.
John Trowbridge,	Cambridge.
A. G. Webster,	Worcester.
Robert W. Willson,	Cambridge.

SECTION III. — 21.

Chemistry.

Samuel Cabot,	Boston.
Arthur M. Comey,	Cambridge.
Thos. M. Drown,	So. Bethlehem, Pa.
Charles W. Eliot,	Cambridge.
Thomas Gaffield,	Boston.
Henry B. Hill,	Cambridge.

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Henry M. Howe,	Boston.
Charles L. Jackson,	Cambridge.
Leonard P. Kinnicutt,	Worcester.
Charles F. Mabery,	Cleveland, O.
Arthur Michael,	Boston.
George D. Moore,	Worcester.
Charles E. Munroe,	Washington.
John U. Nef,	Chicago.
Robert H. Richards,	Boston.
Theodore W. Richards,	Cambridge.
Charles R. Sanger,	St. Louis.
Stephen P. Sharples,	Cambridge.
Francis H. Storer,	Boston.
Charles H. Wing,	Ledger, N. C.
Edward S. Wood,	Boston.

SECTION IV. — 13.

Technology and Engineering.

Eliot C. Clarke,	Boston.
Gaetano Lanza,	Boston.
E. D. Leavitt,	Cambridgeport.
William R. Livermore,	Boston.
Hiram F. Mills,	Lowell.
Cecil H. Peabody,	Boston.
Alfred P. Rockwell,	Manchester.
Andrew H. Russell,	Rock Island, Ill.
Peter Schwamb,	Arlington.
Charles S. Storrow,	Boston.
George F. Swain,	Boston.
William Watson,	Boston.
Morrill Wyman,	Cambridge.

CLASS II. — *Natural and Physiological Sciences.* — 63.

SECTION I. — 13.

Geology, Mineralogy, and Physics of the Globe.

H. H. Clayton,	Milton.
Algernon Coolidge,	Boston.
William O. Crosby,	Boston.
William M. Davis,	Cambridge.
Benj. K. Emerson,	Amherst.
O. W. Huntington,	Cambridge.
Robert T. Jackson,	Boston.
Jules Marcou,	Cambridge.
William H. Niles,	Cambridge.
John E. Pillsbury,	Boston.
Nathaniel S. Shaler,	Cambridge.
Warren Upham,	Cleveland, O.
John E. Wolff,	Cambridge.

SECTION II. — 9.

Botany.

William G. Farlow,	Cambridge.
Charles E. Faxon,	Boston.
George L. Goodale,	Cambridge.
H. H. Hunnewell,	Wellesley.
B. L. Robinson,	Cambridge.
Charles S. Sargent,	Brookline.
Arthur B. Seymour,	Cambridge.
Charles J. Sprague,	Boston.
Roland Thaxter,	Cambridge.

SECTION III. — 25.

Zoölogy and Physiology.

Alexander Agassiz,	Cambridge.
Robert Amory,	Boston.
James M. Barnard,	Milton.
Henry P. Bowditch,	Boston.
William Brewster,	Cambridge.
Louis Cabot,	Brookline.
Samuel F. Clarke,	Williamstown.
W. T. Councilman,	Boston.
Charles B. Davenport,	Cambridge.
Harold C. Ernst,	Boston.
J. Walter Fewkes,	Boston.
Edward G. Gardiner,	Boston.
Samuel Henshaw,	Cambridge.
Alpheus Hyatt,	Cambridge.
John S. Kingsley,	Somerville.
Theodore Lyman,	Brookline.
Edward L. Mark,	Cambridge.
Charles S. Minot,	Boston.
Edward S. Morse,	Salem.
George H. Parker,	Cambridge.
James J. Putnam,	Boston.
Samuel H. Scudder,	Cambridge.
William T. Sedgwick,	Boston.
James C. White,	Boston.
William M. Woodworth,	Cambridge.

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SECTION IV. — 16.

Medicine and Surgery.

Samuel L. Abbot,	Boston.
Edward H. Bradford,	Boston.
Arthur T. Cabot,	Boston.
David W. Cheever,	Boston.
Benjamin E. Cotting,	Roxbury.
Frank W. Draper,	Boston.
Thomas Dwight,	Boston.
Reginald H. Fitz,	Boston.
Charles F. Folsom,	Boston.
Frederick I. Knight,	Boston.
Francis Minot,	Boston.
Samuel J. Mixter,	Boston.
W. L. Richardson,	Boston.
Theobald Smith,	Boston.
Henry P. Walcott,	Cambridge.
John C. Warren,	Boston.

CLASS III. — *Moral and Political Sciences.* — 59.

SECTION I. — 10.

Philosophy and Jurisprudence.

James B. Ames,	Cambridge.
Charles C. Everett,	Cambridge.
Horace Gray,	Boston.
John C. Gray,	Boston.
G. Stanley Hall,	Worcester.
Nathaniel Holmes,	Cambridge.
John E. Hudson,	Boston.
John Lowell,	Newton.
Josiah Royce,	Cambridge.
James B. Thayer,	Cambridge.

SECTION II. — 21.

Philology and Archæology.

William S. Appleton,	Boston.
Charles P. Bowditch,	Boston.
Lucien Carr,	Cambridge.
Franklin Carter,	Williamstown.
Joseph T. Clarke,	Boston.
Henry G. Denny,	Boston.
Epes S. Dixwell,	Cambridge.
William Everett,	Quincy.
William W. Goodwin,	Cambridge.
Henry W. Haynes,	Boston.
David G. Lyon,	Cambridge.
Bennett H. Nash,	Boston.
Frederick W. Putnam,	Cambridge.
Edward Robinson,	Boston.
F. B. Stephenson,	Boston.
Joseph H. Thayer,	Cambridge.
Crawford H. Toy,	Cambridge.
John W. White,	Cambridge.
Justin Winsor,	Cambridge.
John H. Wright,	Cambridge.
Edward J. Young,	Waltham.

SECTION III. — 16.

Political Economy and History.

Charles F. Adams,	Lincoln.
Edward Atkinson,	Boston.
Mellen Chamberlain,	Chelsea.
John Cummings,	Woburn.
Andrew M. Davis,	Cambridge.
Charles F. Dunbar,	Cambridge.
Samuel Eliot,	Boston.
John Fiske,	Cambridge.
A. C. Goodell, Jr.,	Salem.
Henry C. Lodge,	Nahant.
Augustus Lowell,	Boston.
John C. Ropes,	Boston.
Denman W. Ross,	Cambridge.
Charles C. Smith,	Boston.
F. W. Taussig,	Cambridge.
Francis A. Walker,	Boston.

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SECTION IV. — 12.

Literature and the Fine Arts.

Francis Bartlett,	Boston.
John Bartlett,	Cambridge.
George S. Boutwell,	Groton.
J. Elliot Cabot,	Brookline.
Francis J. Child,	Cambridge.
T. W. Higginson,	Cambridge.
S. R. Koehler,	Boston.
Charles G. Loring,	Boston.
Percival Lowell,	Brookline.
Charles Eliot Norton,	Cambridge.
Horace E. Scudder,	Cambridge.
Barrett Wendell,	Boston.

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ASSOCIATE FELLOWS. — 96.

(Number limited to one hundred. Elected as vacancies occur.)

Class I. — *Mathematical and Physical Sciences.* — 38.

Section I. — 16.

Mathematics and Astronomy.

Edward E. Barnard,	Chicago.
S. W. Burnham,	Chicago.
George Davidson,	San Francisco.
Fabian Franklin,	Baltimore.
Asaph Hall,	Washington.
George W. Hill,	Washington.
E. S. Holden,	San José, Cal.
James E. Keeler,	Allegany, Pa.
Emory McClintock,	New York.
Simon Newcomb,	Washington.
H. A. Newton,	New Haven.
Charles L. Poor,	Baltimore.
William A. Rogers,	Waterville, Me.
George M. Searle,	Washington.
J. N. Stockwell,	Cleveland, O.
Chas. A. Young,	Princeton, N.J.

Section II. — 7.

Physics.

Carl Barus,	Washington.
J. Willard Gibbs,	New Haven.
S. P. Langley,	Washington.
A. M. Mayer,	Hoboken, N. J.
A. A. Michelson,	Chicago.
Ogden N. Rood,	New York.
H. A. Rowland,	Baltimore.

Section III. — 8.

Chemistry.

Wolcott Gibbs,	Newport.
Frank A. Gooch,	New Haven.
S. W. Johnson,	New Haven.
M. Carey Lea,	Philadelphia.
J. W. Mallet,	Charlottesville, Va.
E. W. Morley,	Cleveland, O.
J. M. Ordway,	New Orleans.
Ira Remsen,	Baltimore.

Section IV. — 7.

Technology and Engineering.

Henry L. Abbot,	New York.
Cyrus B. Comstock,	Washington.
W. P. Craighill,	Washington.
F. R. Hutton,	New York.
George S. Morison,	Chicago.
William Sellers,	Philadelphia.
Robt. S. Woodward,	New York.

Class II. — *Natural and Physiological Sciences.* — 31.

Section I. — 15.

Geology, Mineralogy, and Physics of the Globe.

Cleveland Abbe,	Washington.
George J. Brush,	New Haven.
Edward S. Dana,	New Haven.
Walter G. Davis,	Cordova, Arg.
Sir J. W. Dawson,	Montreal.
G. K. Gilbert,	Washington.
James Hall,	Albany, N.Y.
Clarence King,	New York.
Joseph LeConte,	Berkeley, Cal.
J. Peter Lesley,	Philadelphia.
J. W. Powell,	Washington.
S. L. Penfield,	New Haven.
R. Pumpelly,	Newport, R.I.
A. R. C. Selwyn,	Ottawa.
G. C. Swallow,	Columbia, Mo.

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SECTION II. — 3.

Botany.

A. W. Chapman,	Apalachicola, Fla.
W. Trelease,	St. Louis.
John D. Smith,	Baltimore.

SECTION III. — 8.

Zoölogy and Physiology.

Joel A. Allen,	New York.
W. K. Brooks,	Baltimore.
George B. Goode,	Washington.
O. C. Marsh,	New Haven.
H. N. Martin,	Baltimore.
S. Weir Mitchell,	Philadelphia.
A. S. Packard,	Providence.
A. E. Verrill,	New Haven.

SECTION IV. — 5.

Medicine and Surgery.

John S. Billings,	Washington.
Jacob M. Da Costa,	Philadelphia.
W. A. Hammond,	New York.
Alfred Stillé,	Philadelphia.
H. C. Wood,	Philadelphia.

CLASS III. — *Moral and Political Sciences.* — 27.

SECTION I. — 5.

Philosophy and Jurisprudence.

T. M. Cooley,	Ann Arbor, Mich.
D. R. Goodwin,	Philadelphia.
Charles S. Peirce,	New York.
T. R. Pynchon,	Hartford, Conn.
Jeremiah Smith,	Cambridge.

SECTION II. — 7.

Philology and Archæology.

A. N. Arnold,	Pawtuxet, R.I.
Timothy Dwight,	New Haven.
B. L. Gildersleeve,	Baltimore.
D. C. Gilman,	Baltimore.
T. R. Lounsbury,	New Haven.
E. E. Salisbury,	New Haven.
A. D. White,	Ithaca, N.Y.

SECTION III. — 9.

Political Economy and History.

Henry Adams,	Washington.
G. P. Fisher,	New Haven.
M. F. Force,	Cincinnati.
H. E. von Holst,	Chicago.
Henry C. Lea,	Philadelphia.
Edward J. Phelps,	Burlington, Vt.
W. G. Sumner,	New Haven.
J. H. Trumbull,	Hartford, Conn.
David A. Wells,	Norwich, Conn.

SECTION IV. — 6.

Literature and the Fine Arts.

James B. Angell,	Ann Arbor, Mich.
L. P. di Cesnola,	New York.
F. E. Church,	New York.
R. S. Greenough,	Florence.
Augustus St. Gaudens,	New York.
W. R. Ware,	New York.

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FOREIGN HONORARY MEMBERS. — 69.

(Number limited to seventy-five. Elected as vacancies occur.)

Class I. — *Mathematical and Physical Sciences.* — 25.

Section I. — 11.

Mathematics and Astronomy.

Arthur Auwers,	Berlin.
Francesco Brioschi.	Milan.
J. H. W. Döllen,	Dorpat.
H. A. E. A. Faye,	Paris.
Hugo Gyldén,	Stockholm.
Charles Hermite,	Paris.
William Huggins,	London.
Otto Struve,	Karlsruhe.
J. J. Sylvester,	Oxford.
H. C. Vogel,	Potsdam.
Karl Weierstrass,	Berlin.

Section II. — 3.

Physics.

A. Cornu.	Paris.
Lord Rayleigh,	Witham.
Sir G. G. Stokes, Bart.,	Cambridge.

Section III. — 8.

Chemistry.

Adolf Baeyer,	Munich.
Marcellin Berthelot,	Paris.
Robert Bunsen.	Heidelberg.
J. H. van't Hoff.	Amsterdam.
Mendeleeff,	St. Petersburg.
Victor Meyer,	Heidelberg.
Sir H. E. Roscoe,	London.
Julius Thomsen,	Copenhagen.

Section IV. — 3.

Technology and Engineering.

Sir Henry Bessemer,	London.
Lord Kelvin,	Glasgow.
Maurice Lévy,	Paris.

Class II. — *Natural and Physiological Sciences.* — 25.

Section I. — 5.

Geology, Mineralogy, and Physics of the Globe.

Alfred Des Cloizeaux,	Paris.
A. E. Nordenskiöld,	Stockholm.
C. F. Rammelsberg,	Berlin.
Henry C. Sorby,	Sheffield.
Heinrich Wild,	Zurich.

Section II. — 7.

Botany.

J. G. Agardh,	Lund.
E. Bornet,	Paris.
Sir Joseph D. Hooker,	Sunningdale.
Baron von Mueller,	Melbourne.
Julius Sachs,	Würzburg.
Solms-Laubach,	Strasburg.
Eduard Strasburger,	Bonn.

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SECTION III. — 9.

Zoölogy and Physiology.

Du Bois-Reymond,	Berlin.
Michael Foster,	Cambridge.
Carl Gegenbauer,	Heidelberg.
Ludimar Hermann,	Königsberg.
Albrecht Kölliker,	Würzburg.
A. Kovalevskij,	St. Petersburg.
Lacaze-Duthiers,	Paris.
Rudolph Leuckart,	Leipsic.
J. J. S. Steenstrup,	Copenhagen.

SECTION IV. — 4.

Medicine and Surgery.

W. Kühne,	Heidelberg.
Sir Joseph Lister, Bart.,	London.
Sir James Paget, Bart.,	London.
Rudolph Virchow,	Berlin.

CLASS III. — *Moral and Political Sciences.* — 19.

SECTION I. — 3.

Philosophy and Jurisprudence.

James Martineau,	London.
Sir Frederick Pollock,	Oxford.
Henry Sidgwick,	Cambridge.

SECTION II. — 7.

Philology and Archæology.

Ingram Bywater,	Oxford.
Sir John Evans,	Hemel Hempstead.
Pascual de Gayangos,	Madrid.
J. W. A. Kirchhoff,	Berlin.
G. C. C. Maspero,	Paris.
Max Müller,	Oxford.
Karl Weinhold,	Berlin.

SECTION III. — 6.

Political Economy and History.

Duc de Broglie,	Paris.
James Bryce,	Oxford.
W. E. Gladstone,	Hawarden.
Hermann Grimm,	Berlin.
Theodor Mommsen,	Berlin.
William Stubbs,	Oxford.

SECTION IV. — 3.

Literature and the Fine Arts.

Jean Léon Gérôme,	Paris.
John Ruskin,	Coniston.
Leslie Stephen,	London.

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STATUTES AND STANDING VOTES.

STATUTES.

Adopted May 30, 1854: *amended September* 8, 1857, *November* 12, 1862, *May* 24, 1864, *November* 9, 1870, *May* 27, 1873, *January* 26, 1876, *June* 16, 1886, *October* 8, 1890, *January* 11 *and May* 10, 1893, *April* 11, *May* 9, *and October* 10, 1894, *and March* 13, *April* 10, *and May* 8, 1895.

CHAPTER I.

Of Fellows and Foreign Honorary Members.

1. The Academy consists of *Fellows* and *Foreign Honorary Members*. They are arranged in three Classes, according to the Arts and Sciences in which they are severally proficient, viz.: Class I. The Mathematical and Physical Sciences; — Class II. The Natural and Physiological Sciences; — Class III. The Moral and Political Sciences. Each Class is divided into four Sections, viz.: Class I., Section 1. Mathematics and Astronomy; — Section 2. Physics; — Section 3. Chemistry; — Section 4. Technology and Engineering. Class II., Section 1. Geology, Mineralogy, and Physics of the Globe; — Section 2. Botany; — Section 3. Zoölogy and Physiology; — Section 4. Medicine and Surgery. Class III., Section 1. Philosophy and Jurisprudence; — Section 2. Philology and Archæology; — Section 3. Political Economy and History; — Section 4. Literature and the Fine Arts.

2. Fellows, resident in the State of Massachusetts, only, may vote at the meetings of the Academy.* Each Resident Fellow shall pay an admission fee of ten dollars and such annual assessment, not exceeding ten dollars, as shall be voted by the Academy at each Annual Meeting.

* The number of Resident Fellows is limited by the Charter to 200.

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3. Fellows residing out of the State of Massachusetts shall be known and distinguished as Associate Fellows. They shall not be liable to the payment of any fees or annual dues, but on removing within the State shall be admitted to the privileges,* and be subject to the obligations, of Resident Fellows. The number of Associate Fellows shall not exceed *one hundred*, of whom there shall not be more than *forty* in either of the three Classes of the Academy.

4. The number of Foreign Honorary Members shall not exceed *seventy-five;* and they shall be chosen from among persons most eminent in foreign countries for their discoveries and attainments in either of the three departments of knowledge above enumerated. And there shall not be more than *thirty* Foreign Members in either of these departments.

CHAPTER II.

Of Officers.

1. There shall be a President, three Vice-Presidents, one for each Class, a Corresponding Secretary, a Recording Secretary, a Treasurer, and a Librarian, which officers shall be annually elected, by ballot, at the Annual Meeting, on the second Wednesday in May.

2. At the same time, and in the same manner, nine Councillors shall be elected, three from each Class of the Academy, but the same Fellows shall not be eligible on more than three successive years. These nine Councillors, with the President, the three Vice-Presidents, the two Secretaries, the Treasurer, and the Librarian, shall constitute the Council. It shall be the duty of this Council to exercise a discreet supervision over all nominations and elections. With the consent of the Fellow interested, they shall have power to make transfers between the several Sections of the same Class, reporting their action to the Academy.

3. If any office shall become vacant during the year, the vacancy shall be filled by a new election, and at the next stated meeting, or at a meeting called for this purpose.

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* Associate Fellows may attend, but cannot vote, at meetings of the Academy. See Chapter I. 2.

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CHAPTER III.

Of Nominations of Officers.

1. At the stated meeting in March, the President shall appoint from the next retiring Councillors a Nominating Committee of three Fellows, one for each class.

2. It shall be the duty of this Nominating Committee to prepare a list of candidates for the offices of President, Vice-Presidents, Corresponding Secretary, Recording Secretary, Treasurer, Librarian, Councillors, and the Standing Committees which are chosen by ballot; and to cause this list to be sent by mail to all the Resident Fellows of the Academy not later than four weeks before the Annual Meeting.

3. Independent nominations for any office, signed by at least five Resident Fellows and received by the Recording Secretary not less than ten days before the Annual Meeting, shall be inserted in the call for the Annual Meeting, which shall then be issued not later than one week before that meeting.

4. The Recording Secretary shall prepare for use, in voting at the Annual Meeting, a ballot containing the names of all persons nominated for office under the conditions given above.

5. When an office is to be filled at any other time than at the Annual Meeting, the President shall appoint a Nominating Committee, in accordance with the provisions of Section 1, which shall announce its nomination in the manner prescribed in Section 2 at least two weeks before the time of election. Independent nominations, signed by at least five Resident Fellows and received by the Recording Secretary not later than one week before the meeting for election, shall be inserted in the call for that meeting.

CHAPTER IV.

Of the President.

1. It shall be the duty of the President, and, in his absence, of the senior Vice-President present, or next officer in order as above enumerated, to preside at the meetings of the Academy; to summon extraordinary meetings, upon any urgent occasion; and to execute or see to the execution of the Statutes of the

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Academy. Length of continuous membership in the Academy shall determine the seniority of the Vice-Presidents.

2. The President, or, in his absence, the next officer as above enumerated, is empowered to draw upon the Treasurer for such sums of money as the Academy shall direct. Bills presented on account of the Library, or the Publications of the Academy, must be previously approved by the respective committees on these departments.

3. The President, or, in his absence, the next officer as above enumerated, shall nominate members to serve on the different committees of the Academy which are not chosen by ballot.

4. Any deed or writing to which the common seal is to be affixed shall be signed and sealed by the President, when thereto authorized by the Academy.

CHAPTER V.

Of Standing Committees.

1. At the Annual Meeting there shall be chosen the following Standing Committees, to serve for the year ensuing, viz.: —

2. The Committee of Finance, to consist of the President, Treasurer, and one Fellow chosen by ballot, who shall have charge of the investment and management of the funds and trusts of the Academy. The general appropriations for the expenditures of the Academy shall be moved by this Committee at the Annual Meeting, and all special appropriations from the general and publication funds shall be referred to or proposed by this Committee.

3. The Rumford Committee, of seven Fellows, to be chosen by ballot, who shall consider and report on all applications and claims for the Rumford Premium, also on all appropriations from the income of the Rumford Fund, and generally see to the due and proper execution of this trust.

4. The C. M. Warren Committee, of seven Fellows, to be chosen by ballot, who shall consider and report on all applications for appropriations from the income of the C. M. Warren Fund, and generally see to the due and proper execution of this trust.

5. The Committee of Publication, of three Fellows, to whom all memoirs submitted to the Academy shall be referred, and to

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whom the printing of memoirs accepted for publication shall be intrusted.

6. The Committee on the Library, of three Fellows, who shall examine the Library, and make an annual report on its condition and management.

7. An Auditing Committee, of two Fellows, for auditing the accounts of the Treasurer.

CHAPTER VI.

Of the Secretaries.

1. The Corresponding Secretary shall conduct the correspondence of the Academy, recording or making an entry of all letters written in its name, and preserving on file all letters which are received; and at each meeting he shall present the letters which have been addressed to the Academy since the last meeting. With the advice and consent of the President, he may effect exchanges with other scientific associations, and also distribute copies of the publications of the Academy among the Associate Fellows and Foreign Honorary Members, as shall be deemed expedient; making a report of his proceedings at the Annual Meeting. Under the direction of the Council for Nomination, he shall keep a list of the Fellows, Associate Fellows, and Foreign Honorary Members, arranged in their Classes and in Sections in respect to the special sciences in which they are severally proficient; and he shall act as secretary to the Council.

2. The Recording Secretary shall have charge of the Charter and Statute-book, journals, and all literary papers belonging to the Academy. He shall record the proceedings of the Academy at its meetings; and after each meeting is duly opened, he shall read the record of the preceding meeting. He shall notify the meetings of the Academy, and apprise committees of their appointment. He shall post up in the Hall a list of the persons nominated for election into the Academy; and when any individual is chosen, he shall insert in the record the names of the Fellows by whom he was nominated.

3. The two Secretaries, with the Chairman of the Committee of Publication, shall have authority to publish such of the proceedings of the Academy as as may seem to them calculated to promote the interests of science.

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CHAPTER VII.

Of the Treasurer.

1. The Treasurer shall give such security for the trust reposed in him as the Academy shall require.

2. He shall receive officially all moneys due or payable, and all bequests or donations made to the Academy, and by order of the President or presiding officer shall pay such sums as the Academy may direct. He shall keep an account of all receipts and expenditures; shall submit his accounts to the Auditing Committee; and shall report the same at the expiration of his term of office.

3. The Treasurer shall keep a separate account of the income and appropriation of the Rumford Fund, and report the same annually.

4. All moneys which there shall not be present occasion to expend shall be invested by the Treasurer, under the direction of the Finance Committee, on such securities as the Academy shall direct.

CHAPTER VIII.

Of the Librarian and Library.

1. It shall be the duty of the Librarian to take charge of the books, to keep a correct catalogue of same, and to provide for the delivery of books from the Library. He shall also have the custody of the publications of the Academy.

2. The Librarian, in conjunction with the Committee on the Library, shall have authority to expend, as they may deem expedient, such sums as may be appropriated, either from the Rumford or the General Fund of the Academy, for the purchase of books, and for defraying other necessary expenses connected with the Library. They shall have authority to propose rules and regulations concerning the circulation, return, and safe-keeping of books; and to appoint such agents for these purposes as they may think necessary.

3. To all books in the Library procured from the income of the Rumford Fund, the Librarian shall cause a stamp or label to be affixed, expressing the fact that they were so procured.

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4. Every person who takes a book from the Library shall give a receipt for the same to the Librarian or his assistant.

5. Every book shall be returned in good order, regard being had to the necessary wear of the book with good usage. And if any book shall be lost or injured, the person to whom it stands charged shall replace it by a new volume or set, if it belongs to a set, or pay the current price of the volume or set to the Librarian; and thereupon the remainder of the set, if the volume belonged to a set, shall be delivered to the person so paying for the same.

6. All books shall be returned to the Library for examination at least one week before the Annual Meeting.

CHAPTER IX.

Of Meetings.

1. There shall be annually four stated meetings of the Academy; namely, on the second Wednesday in May (the Annual Meeting), on the second Wednesday in October, on the second Wednesday in January, and on the second Wednesday in March. At these meetings only, or at meetings adjourned from these and regularly notified, shall appropriations of money be made, or alterations of the statutes or standing votes of the Academy be effected.

2. Fifteen Fellows shall constitute a quorum for the transaction of business at a stated meeting. Seven Fellows shall be sufficient to constitute a meeting for scientific communications and discussions.

3. The Recording Secretary shall notify the meetings of the Academy to each Fellow residing in Boston and the vicinity; and he may cause the meetings to be advertised, whenever he deems such further notice to be needful.

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CHAPTER X.

Of the Election of Fellows and Honorary Members.

1. Elections shall be made by ballot, and only at stated meetings.

2. Candidates for election as Resident Fellows must be proposed by two or more Resident Fellows, in a recommendation signed by them, specifying the Section to which the nomination is made, which recommendation shall be transmitted to the Corresponding Secretary, and by him referred to the Council for Nomination. No person recommended shall be reported by the Council as a candidate for election, unless he shall have received a written approval, signed at a meeting of the Council by at least seven of its members. All nominations thus approved shall be read to the Academy at a stated meeting, and shall then stand on the nomination list during the interval between two stated meetings, and until the balloting. No person shall be elected a Resident Fellow, unless he shall have been resident in this Commonwealth one year next preceding his election. If any person elected a Resident Fellow shall neglect for one year to pay his admission fee, his election shall be void; and if any Resident Fellow shall neglect to pay his annual assessments for two years, provided that his attention shall have been called to this article, he shall be deemed to have abandoned his Fellowship; but it shall be in the power of the Treasurer, with the consent of the Council, to dispense (*sub silentio*) with the payment both of the admission fee and of the assessments, whenever in any special instance he shall think it advisable so to do.

3. The nomination of Associate Fellows shall take place in the manner prescribed in reference to Resident Fellows; and after such nomination shall have been publicly read at a stated meeting previous to that when the balloting takes place, it shall be referred to the Council for Nomination; and a written approval, authorized and signed at a meeting of said Council by at least seven of its members, shall be requisite to entitle the candidate to be balloted for. The Council may in like manner originate nominations of Associate Fellows, which must be read at a stated meeting previous to the election, and be exposed on the nomination list during the interval.

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4. Foreign Honorary Members shall be chosen only after a nomination made at a meeting of the Council, signed at the time by at least seven of its members, and read at a stated meeting previous to that on which the balloting takes place.

5. Three fourths of the ballots cast must be affirmative, and the number of affirmative ballots must amount to eleven to effect an election of Fellows or Foreign Honorary Members.

6. Each Section of the Academy is empowered to present lists of persons deemed best qualified to fill vacancies occurring in the number of Foreign Honorary Members or Associate Fellows allotted to it; and such lists, after being read at a stated meeting, shall be referred to the Council for Nomination.

7. If, in the opinion of a majority of the entire Council, any Fellow — Resident or Associate — shall have rendered himself unworthy of a place in the Academy, the Council shall recommend to the Academy the termination of his Fellowship; and provided that a majority of two thirds of the Fellows at a stated meeting, consisting of not less than fifty Fellows, shall adopt this recommendation, his name shall be stricken off the roll of Fellows.

CHAPTER XI.

Of Amendments of the Statutes.

1. All proposed alterations of the Statutes, or additions to them, shall be referred to a committee, and, on their report at a subsequent meeting, shall require for enactment a majority of two thirds of the members present, and at least eighteen affirmative votes.

2. Standing Votes may be passed, amended, or rescinded, at any stated meeting, by a majority of two thirds of the members present. They may be suspended by a unanimous vote.

CHAPTER XII.

Of Literary Performances.

1. The Academy will not express its judgment on literary or scientific memoirs or performances submitted to it, or included in its publications.

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STANDING VOTES.

1. Communications of which notice had been given to the Secretary shall take precedence of those not so notified.

2. Resident Fellows who have paid all fees and dues chargeable to them are entitled to receive one copy of each volume or article printed by the Academy, on application to the Librarian personally or by written order, within two years from the date of publication. And the current issues of the Proceedings shall be supplied, when ready for publication, free of charge, to all the Fellows and members of the Academy who desire to receive them.

3. The Committee of Publication shall fix from time to time the price at which the publications of the Academy may be sold. But members may be supplied at half this price with volumes which they are not entitled to receive free, and which are needed to complete their sets.

4. Two hundred extra copies of each paper accepted for publication in the Memoirs or Proceedings of the Academy shall be placed at the disposal of the author, free of charge.

5. Resident Fellows may borrow and have out from the Library six volumes at any one time, and may retain the same for three months, and no longer.

6. Upon special application, and for adequate reasons assigned, the Librarian may permit a larger number of volumes, not exceeding twelve, to be drawn from the Library for a limited period.

7. Works published in numbers, when unbound, shall not be taken from the Hall of the Academy, except by special leave of the Librarian.

8. Books, publications, or apparatus shall be procured from the income of the Rumford Fund only on the certificate of the Rumford Committee that they, in their opinion, will best facilitate and encourage the making of discoveries and improvements which may merit the Rumford Premium.

9. The Annual Meeting and the other stated meetings shall be holden at eight o'clock, P. M.

10. A meeting for receiving and discussing scientific communications may be held on the second Wednesday of each month not appointed for stated meetings, excepting July, August, and September.

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RUMFORD PREMIUM.

In conformity with the terms of the gift of Benjamin, Count Rumford, granting a certain fund to the American Academy of Arts and Sciences, and with a decree of the Supreme Judicial Court for carrying into effect the general charitable intent and purpose of Count Rumford, as expressed in his letter of gift, the Academy is empowered to make from the income of said fund, as it now exists, at any Annual Meeting, an award of a gold and silver medal, being together of the intrinsic value of three hundred dollars, as a premium to the author of any important discovery or useful improvement in light or in heat, which shall have been made and published by printing, or in any way made known to the public, in any part of the continent of America, or any of the American islands; preference being always given to such discoveries as shall, in the opinion of the Academy, tend most to promote the good of mankind; and to add to such medals, as a further premium for such discovery and improvement, if the Academy see fit so to do, a sum of money not exceeding three hundred dollars.

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